982. *Syntheses of Substituted Amino-, Aminovinyl-, and Aminobutadienyl-p-quinones.*

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Dialkylaminovinylquinones can often be synthesised in good yield from halogenated quinones, acetaldehyde, and secondary amines, isolation of the enamines being unnecessary. A dialkylaminobutadienyl-quinone has been prepared in the naphthalene series, by using 1-diethylaminobutadiene or, less efficiently, a mixture of diethylamine and crotonaldehyde. Replacement of chlorine in the blue dialkylaminovinyltrichlorobenzoquinones can lead to purple or green compounds. For comparison, some reactions between quinones and primary and secondary amines have been carried out. The light absorption properties of these coloured compounds are discussed; it is considered that the side-chains, $(CH{=}CH)_{1-2}{\cdot}NR_2$, in the new quinones are of *trans*-geometry.

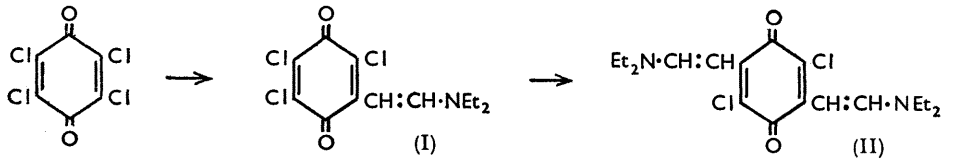
In the preceding paper,[1] the formation of coloured dialkylaminovinyl-quinones from quinones and simple tertiary amines containing *N*-ethyl groups was recorded. The second stage of these reactions was considered to be the condensation of an enamine ($R_2N{\cdot}CH{:}CH_2$) with the starting quinone; it is with the further study of this coupling reaction that the present paper is concerned.

Though the original intention was to prepare diethylvinylamine * from diethylamine and acetaldehyde and condense it with chloranil, it was found that the deep blue colour of the diethylaminovinyl-quinone (I) was rapidly produced on successively adding the aldehyde and the secondary amine to a solution of the quinone, and preparation of the (probably unstable) enamine was not therefore necessary. The reaction between chloranil, diethylamine, and acetaldehyde (molar ratios 1 : 2 : 1) in benzene at room temperature was complete within 10 minutes, and the blue quinone (I) (identical with that previously

* Its preparation by another method has been claimed by Meyer and Hopff.[2]

[1] Buckley, Dunstan, and Henbest, preceding paper.
[2] Meyer and Hopff, *Ber.*, 1921, **54**, 2274.

obtained from triethylamine) was readily isolated in 80% yield. The speed of formation and condensation of the enamine is therefore greater than that of reaction between the quinone and the secondary amine, leading to the replacement of chlorine by a diethylamino-group.

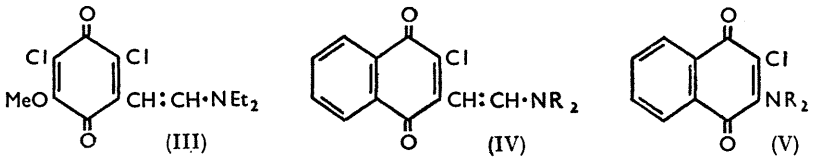


(I) (II)

With further amounts of acetaldehyde and diethylamine the blue quinone (I) was converted into the purple bisdiethylaminovinyl-quinone (II); the *p*-orientation of the new substituents is suggested by analogy with the reactions of chloranil and related quinones with other nucleophilic reagents (cf. below).

Blue compounds related to the quinone (I) have been obtained also from dimethylamine, morpholine, pyrrolidine, piperidine, hexamethyleneimine, diethanolamine, and methylaniline.

As a rule those quinones which react with a primary amine also react with a mixture of acetaldehyde and diethylamine to give diethylaminovinyl-quinones. Thus, in keeping with the reaction with *n*-butylamine (below), a methoxyl group is replaced from 2 : 6-dichloro-3 : 5-dimethoxybenzoquinone, and the blue quinone (III) is produced. 2 : 3-Dichloronaphthaquinone, acetaldehyde, and diethylamine gave the purple compound (IV; R = Et) (94%), previously obtained in low yield from triethylamine. The nitrogen atom in dimethylamine is less shielded than that in diethylamine, so in this reaction the former amine gave also an appreciable amount of the red dimethylamino-quinone (V; R = Me) and less (35%) of the dimethylaminovinyl compound (IV; R = Me).

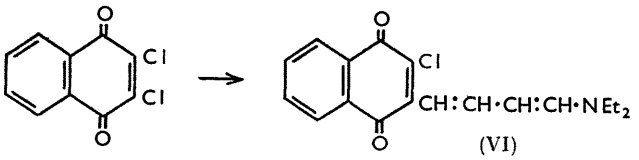


(III) (IV) (V)

Qualitative tests with acetaldehyde and diethylamine showed that many other quinones formed purple–blue solutions. *p*-Benzoquinone gave a purple solution but the product was hard to purify.

Tests with diethylamine and chloranil showed that aldehydes, $R{\cdot}CH_2{\cdot}CHO$, usually gave blue solutions, but the colours were weaker and the blue compounds more reactive and difficult to isolate by conventional techniques. The results described in this and the following paper show that the ease of the coupling reaction decreases in the order, $CH_2{:}CH{\cdot}NR_2$, *cis*-$CH{:}CH{\cdot}NR_2$, *trans*-$CH{:}CH{\cdot}NR_2$. These aldehydes and secondary amines would be expected to generate largely or wholly *trans*-enamines (cf. infrared evidence below).

The synthesis probably cannot be extended to ketones, as the attempted reaction of acetone with chloranil and morpholine led only to replacement of chlorine by morpholine residues.



(VI)

A compound with a more extended chromophore was also prepared. 2 : 3-Dichloronaphthaquinone, crotonaldehyde, and diethylamine gave 20% of the blue compound (VI),

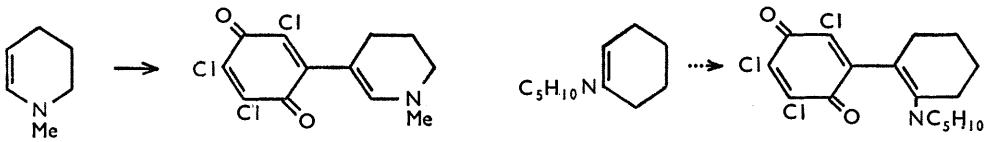
with a larger amount of the product formed by replacement of one chlorine by a diethylamino-residue. The presumed intermediate, $CH_2{:}CH{\cdot}CH{:}CH{\cdot}NEt_2$, can be readily prepared,[3] and gave the same blue compound (VI) in 80% yield in 3 min. at room temperature. It is possible that the reactions are assisted by complex formation between the quinone and the unsaturated amine (cf. preceding paper).

In general, the reactions between chloro-quinones, acetaldehyde, and secondary amines were rapid, often being complete in less than 10 minutes at room temperature. Since dehydration is involved in the formation of the enamine, it is noteworthy that the blue quinone was formed also in aqueous dioxan.

Configuration of the Side-chain, and Infrared Absorption of the New Quinones.—The methods used to give the quinones with $(CH{:}CH)_{1-2}{\cdot}NR_2$ side-chains would be expected to afford the more extended, and probably more stable, *trans*-compounds, and the following observations support this assignment.

The enamine (VII) generated by dehydrogenation of 1-methylpiperidine (following paper) yields a blue quinone (VIII), in which the chromophoric substituents must be *trans* in the side-chain. Apart from expected minor differences, the ultraviolet absorption of the quinone (VIII) was similar to that of related compounds with a $CH{:}CH{\cdot}NR_2$ substituent. In contrast, the reaction between the enamine (IX) and chloranil, which in theory could give a compound with a *cis*-chromophoric group (*i.e.*, X), gave a colourless solution: this reaction is being further studied, but there is no evidence that the quinone (X) is formed.

Each of the quinones containing a $CH{:}CH{\cdot}NR_2$ substituent exhibited an infrared band near 960 cm.$^{-1}$. That this is due to a *trans*-double bond is supported by the fact that the butadienyl-quinone (VI) and the bisdialkylaminovinyl-quinone (II) gave absorption bands at 963 and 958 cm.$^{-1}$ respectively, of approximately double the intensity. (The simpler enamine, $[CH_2]_5 > N{\cdot}CH{:}CHEt$, prepared from piperidine and *n*-butyraldehyde,[4] exhibited a band of medium strength at 940 cm.$^{-1}$, consistent with the presence of a *trans*-double bond.)



(VII) (VIII) (IX) (X)

Quinones with an unsaturated amine side-chain, *e.g.*, (I), (IV), and (VI), gave two carbonyl bands, one of normal intensity and position (~1670 cm.$^{-1}$) for a quinone and the other of lower intensity and frequency (~1640 cm.$^{-1}$). The latter probably represents the carbonyl group conjugated with the unsaturated side-chain.

Some Reactions of Dialkylaminovinylquinones with Nucleophiles.—Owing to the presence of chlorine *para* to the unsaturated side-chain, blue quinones such as (I) react readily with nucleophilic reagents such as amines or dilute alkali. Thus, the disubstituted quinone (II) was formed from (I) with an excess of acetaldehyde and the secondary amine, whereas the naphthaquinone (IV) was not substituted further under the same conditions.

Reactions of the blue quinone (XI) with a primary (*n*-butylamine) and a secondary amine (dimethylamine) proceeded differently. An excess of the latter amine led to the quinone (XII) by replacement of the *p*-chlorine atom. Reaction with *n*-butylamine was also rapid, both a chlorine and the morpholine residue being replaced by butylamino-groups, so the compound is formulated as (XIII).

Under the same conditions, secondary amine residues in the side-chains of the quinones (IV), (VI), and (XII) were not displaced by *n*-butylamine, so the unusual step in the

[3] Bowden, Braude, Jones, and Weedon, *J.*, 1946, 45.
[4] Mannich and Davidsen, *Ber.*, 1936, **69**, 2106.

TABLE 1. *Absorption maxima* (Å, *with* ε *in parentheses*) *of* p-*benzoquinones in pure dioxan at* 2200—8000 Å.

No.	Subst. at position 2	3	5	6	Band I	Band II	Band III
Dimethoxy- and diamino-quinones							
1	H	MeO	H	MeO	—	2770 (17,300)	3600 (320)
2	Cl	MeO	Cl	MeO	—	3000 (13,300)	4040 (360)
3	MeO	H	H	MeO	—	2850 (17,200)	3670 (760)
4	MeO	Cl	Cl	MeO	—	2960 (12,300)	4050 (380)
5	H	NHBu	H	NHBu	—	3310; 3420 (30,600; 31,800)	4760 (270)
6	Cl	NHBu	H	NHBu	—	3480 (31,400)	4980 (300)
7	Cl	NHBu	Cl	NHBu	2240 (18,200)	3550 (25,300)	5200 (230)
8	MeO	NHBu	H	NHBu	—	3490 (22,000)	5380 (300)
9	MeO	NHBu	Cl	NHBu	2250 (21,300)	3570 (25,600)	5480 (270)
10	H	NMe_2	H	NMe_2	2220 (25,200)	3620 (22,500)	4950 (410)
11	Cl	NMe_2	Cl	NMe_2	2380 (15,900)	4140 (10,100)	—
12	H	OC_4H_8N	H	OC_4H_8N	2260 (24,600)	3680 (18,400)	5010 (570)
13	Cl	OC_4H_8N	Cl	OC_4H_8N	2410 (17,700)	4350 (11,200)	—
Amino-quinones							
14	Cl	Cl	Cl	NMe_2	2440 (14,400)	3050, 3110 (5800)	5450 (2300)
15	Cl	Cl	Cl	OC_4H_8N	2460 (15,100)	3190 (4800)	5450 (2900)
16	MeO	Cl	Cl	NHBu	2260 (17,400)	3140 (8950)	5150 (1500)
Dialkylaminovinyl-quinones							
17	Cl	Cl	Cl	$C_2H_2{\cdot}NMe_2$	2420 (7500)	3140 (29,300)	6300 (8500)
18	Cl	Cl	Cl	$C_2H_2{\cdot}NEt_2$	2410 (9700)	3160 (30,500)	6450 (8800)
19	Cl	Cl	Cl	$C_2H_2{\cdot}N<[CH_2]_4$	2430 (6700)	3160 (27,500)	6600 (8200)
20	Cl	Cl	Cl	$C_2H_2{\cdot}N<[CH_2]_5$	2420 (7800)	3160 (32,000)	6420 (9200)
21	Cl	Cl	Cl	$C_2H_2{\cdot}N<[CH_2]_6$	2400 (7500)	3180 (28,300)	6450 (8400)
22	Cl	Cl	Cl	$C_2H_2{\cdot}NMePh$	2470 (8850)	3240 (28,500)	6350 (10,300)
23	Cl	Cl	Cl	$C_2H_2{\cdot}NC_4H_8O$	2430 (5560)	3150 (22,100)	6300 (6700)
24	Cl	Cl	Cl	1 : 4 : 5 : 6-Tetrahydro-1-methylpyridyl	2570 (9300)	3250 (16,700)	7050 (8000)

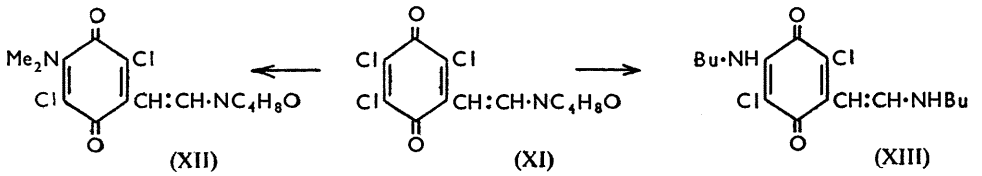
Position:	2	3	5	6	Band: I	II	II A	III
25	MeO	Cl	Cl	$C_2H_2{\cdot}NEt_2$	—	3150 (26,600)	—	6350 (7000)
26	Cl	MeO	Cl	$C_2H_2{\cdot}NEt_2$	—	3110 (26,300)	3720 (6400)	6300 (9100)
27	Cl	NHBu	Cl	$C_2H_2{\cdot}NHBu$	2260 (8550)	2960 (18,500)	4320 (25,000)	6200 (5100)
28	Cl	NMe_2	Cl	$C_2H_2{\cdot}NC_4H_8O$	2390 (14,100)	3060 (24,800)	4680 (21,600)	6300 (3800)
29	Cl	$C_2H_2{\cdot}NEt_2$	Cl	$C_2H_2{\cdot}NEt_2$	2410 (10,000)	3360 (30,300)	5370 (27,700)	6450 (4000)

TABLE 1. (*Continued.*)

Naphthaquinones

Position	2	3	Band: I	II	III
30	Cl	NHEt	2370 (12,800)	2750 (22,100)	4660 (3000)
31	Cl	NMe_2	2470 (13,000)	2820 (14,500)	4760 (3100)
32	Cl	NEt_2	2470 (14,800)	2830 (12,800)	4940 (3100)
33	Cl	OC_4H_8N	2480 (14,200)	2820 (16,000)	4880 (4200)
34	H	OC_4H_8N	2380 (14,200)	2710 (17,400)	4440 (3450)
35	Cl	$C_2H_2{\cdot}NMe_2$	2380 (10,100)	3210 (26,600)	5580 (12,200)
36	Cl	$C_2H_2{\cdot}NEt_2$	2380 (10,200)	3230 (27,600)	5640 (13,300)
37	Cl	$C_4H_4{\cdot}NEt_2$	2460 (16,000)	3650 (34,200)	6250 (29,900)

formation of (XIII) is due to the NHR grouping in the presumed initial product formed by replacement of *p*-chlorine. This initial product can possibly occur in an *o*-quinonoid form, whose greater reactivity results in amine replacement on the side-chain. [The high reactivity of *o*-quinones is well known. In a simple competitive reaction between *o*- and *p*-chloranils and *n*-butylamine (molar ratios 1 : 1 : 2), the *p*-quinone (89%) but no



(XII) (XI) (XIII)

o-quinone was recovered.] The quinones (XII) and (XIII) gave respectively dull green and brilliant green solutions in organic solvents (cf. below).

Light Absorption.—The solvent properties and unreactivity of purified dioxan made this a suitable medium for the determination of the ultraviolet and visible absorption of the present compounds. Most of the quinones show three bands, referred to as bands I, II, and III (see Table 1).

The general bathochromic effect of chlorine is apparent (pairs 1–2, 3–4, 5–7, 34–33). The visual effect in the last pair is the change in colour from orange to red.

Band I. Variation of the side-chain from dialkylamino- to dialkylaminovinyl or dialkylaminobutadienyl cause only small variations in the position of this band (nos. 14 and 17; 32, 36, and 37).

Band II. The position of this band is influenced by conjugation of the quinone system with electron-donating side-chains. Thus in the naphthaquinone series, $\lambda_{max.}$ rises for the substitutent order, NHEt, NEt_2, $Et_2N{\cdot}CH{:}CH$, $Et_2N{\cdot}[CH{:}CH]_2$ (nos. 30, 33, 36, 37). In the benzoquinone series the position of the band does not greatly change but the intensity may be trebled on replacement of an amine substituent (nos. 14—16) by a dialkylaminovinyl group (nos. 17—24). In 3 : 6-bisaminosubstituted benzoquinones, $\lambda_{max.}$ increases and ε decreases on progression from bisbutylamino- (nos. 5 and 7) to bisdimethylamino-compounds (nos. 10 and 11). For such alterations in the alkyl substituents, these changes are larger than expected; the absorption of the bisbutylamino-compounds may however be somewhat " abnormal " owing to hydrogen bonding to the carbonyl groups which would give larger resonance contributions from the quinoneimide form. In fact, these bisbutylamino-compounds (nos. 5—9) and the green quinone no. 27 could be formulated alternatively as (hydrogen-bonded) quinoneimides. Until further details concerning the

hydrogen positions are available, the compounds are written in the usual quinonoid forms (cf. formulæ XIII, XIV, XX, XXII, and XXIV). Steric inhibition of resonance may contribute to the lowered intensities of band II in the chlorinated compounds (nos. 11 and 13) and also to the decreasing intensity of this band in the compounds nos. 30, 31, and 32.

Band III. In many of the compounds this absorption band largely determines the colour of the quinone. Single absorption bands in the visible region cause the monoaminobenzoquinones (nos. 14—16) to be purple and the dialkylaminovinyl compounds (nos. 17—24) to be blue in solution. Band III (and also the ultraviolet band II) is at a shorter wavelength in naphthaquinones than in related benzoquinones, and the monoamino-compounds (nos. 30—32) are red, the dialkylaminovinylquinones (nos. 35 and 36) are purple, and the dialkylaminobutadienyl-quinone (no. 37) is blue.

The red to red-brown diaminobenzoquinones show either no selective visible absorption (nos. 11 and 13) or bands of relatively low intensity near 5000 Å (nos. 5—10 and 12).

The absorption maximum (band III) of dialkylaminovinyl-quinones varies in the expected manner with changes in alkyl substituents. Changes from dimethylamino to diethylamino (nos. 17 and 18), and from piperidino to pyrrolidino (nos. 19 and 20), cause $\lambda_{max.}$ to move to longer wavelengths. The compound no. 24 contains an extra *C*-alkyl group in the side-chain, and $\lambda_{max.}$ moves to 7050 Å.

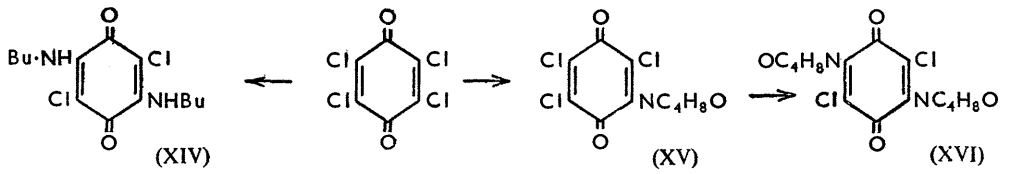
Band IIA. The compounds nos. 26—29 contain an electron-donating substituent *para* to a dialkylaminovinyl side-chain, and each shows an additional band (labelled IIA) between bands II and III (the compound no. 25 with a methoxyl group *meta* to the side-chain does not give a fourth band). In these compounds the band near 6400 Å normally responsible for a blue colour does not vary appreciably, but the position of band IIA moves to a longer wavelength and into the visible region as conjugation increases in the order MeO, NHBu, $Et_2N{\cdot}CH{:}CH$. The consequence is that the quinones nos. 27 and 28 give green solutions, and the bisdialkylaminovinyl compound no. 29 is purplish in solution.

TABLE 2. *Variation of the long-wave absorption maximum* (Å, *with* ε *in parentheses*) *of 2-chloro-3-2′-diethylaminovinylnaphthaquinone* (IV) *with solvent.*

*cyclo*Hexane	5450 (12,500)	Pyridine	5750 (13,000)
Dioxan	5640 (13,300)	Propan-2-ol	5800 (13,300)
Benzene	5700 (13,200)	Nitromethane	5850 (13,300)
Acetone	5750 (13,700)	Pyridine–water (9 : 1)	5850 (13,200)

The absorption maximum, in the visible region, of the dialkylaminovinylnaphthaquinone (IV) moves to longer wavelength in the usual way with increasing polarity of solvent (Table 2); the compounds are not sufficiently polarised to give the (reverse) effect described by Brooker, Keyes, and Heseltine.[5]

Reactions of Quinones with Primary and Secondary Amines.—Many examples of such reactions have been described previously;[6,7] the following experiments were carried out in order to supplement and amplify the present work, involving the less well-known enamines as nucleophilic reagents.

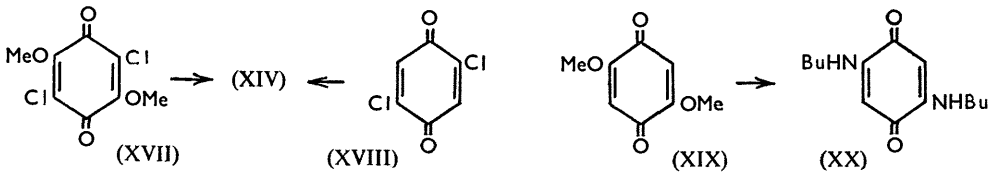


The reaction of chloranil with *n*-butylamine paralleled the formation of the green quinone (XIII) from the quinone (XI) in that a disubstituted product (XIV) was obtained—even when a deficiency of amine was used. Reactions between chloranil and

[5] Brooker, Keyes, and Heseltine, *J. Amer. Chem. Soc.*, 1951, **73**, 5350.
[6] Fieser, *ibid.*, 1926, **48**, 2936.
[7] Anslow and Raistrick, *J.*, 1939, 1446.

different proportions of the secondary amine, morpholine, gave the substituted quinones (XV) and (XVI).

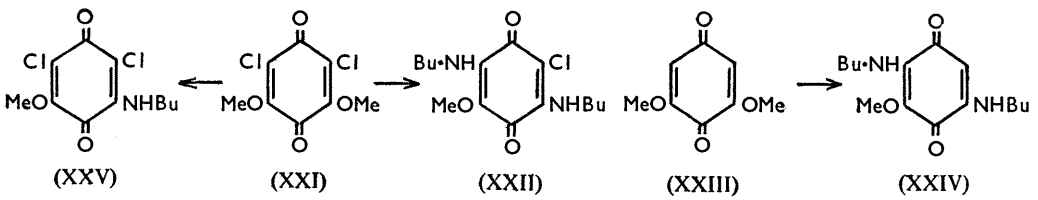
In the formation of the blue quinone (III) it was observed that methoxyl, not chlorine, was displaced by an enamine grouping (as already observed in the naphthaquinone series [6]). The reaction of the dichlorodimethoxyquinone (XVII) with the *n*-butylamine similarly gave the diamine (XIV) in high yield and the formation of chloride ion could not be detected. Quinones containing adjacent hydrogen and chlorine substituents are attacked by amines (and by enamines—see following paper) at either position. Thus the sparingly soluble quinone (XIV) was isolated in low yield after reaction of the dichloroquinone (XVIII) with *n*-butylamine, but replacement of chlorine occurred simultaneously (silver test). In these examples the replacement of methoxyl or hydrogen from positions adjacent to chlorine substituents appears to be facilitated by the electron-attracting properties of the halogen group.



Compared with the formation of the diamino-quinone (XIV) from the dichlorodimethoxyquinone (XVII) the rate of formation of the unchlorinated analogue (XX) from the dimethoxy-quinone (XIX) was very slow; this may in part be due to poorer complex association between the amine and the unchlorinated dimethoxyquinone.

The above and earlier work show that reactions of benzoquinones with an excess of primary amine commonly lead to *para*-disubstituted products. The reactions of the dimethoxy-quinones (XXI) and (XXIII) with *n*-butylamine provide further examples, the products (XXII) and (XXIV) being obtained, but more slowly.

However, the dichlorodimethoxy-quinone (XXI) differed from its isomer (XVII) in that a (purple) monosubstituted compound could be isolated when less butylamine was used. Analyses confirmed that a methoxyl group had been displaced, the product having the structure (XXV). It is not difficult to see why the monosubstituted compound (XXV) was readily obtained whereas its isomer from (XVII) was further substituted. In (XXV)



the methoxyl and butylamino-groups are in a cross-conjugated arrangement and the polarisation necessary for the second stage in the reaction is opposed by the methoxyl group. In the monosubstituted compound from (XVII) the systems MeO·C:C·C:O and Bu·NH·C:C·C:O are separated by single bonds, and mutual polarisation (leading on the methoxyl side to displacement of this group) of the systems is encouraged.

Experimental

Compounds whose light absorptions are recorded in the Tables are either described in this group of papers or were prepared by known methods.

General Procedure for the Preparation of Dialkylaminovinyl-quinones.—The secondary amine (2 mol.) was added to a stirred solution of the quinone (1 mol.) and freshly distilled acetaldehyde (1 mol.) in benzene at 20—25° in the presence of a few grams of anhydrous sodium sulphate (this was not essential but improved the yields of blue quinones). After 10 min., 0·5N-sulphuric

acid was added to extract amine salts, and the benzene layer was dried and concentrated under reduced pressure. The solution of the coloured quinone was filtered through a small amount of neutralised, deactivated alumina,[8] and the product was crystallised. More extensive chromatography on the same adsorbent was sometimes necessary.

2 : 3 : 5-*Trichloro*-6-2′-*diethylaminovinylbenzoquinone* (I).—The reaction between diethylamine (0·73 g.), acetaldehyde (0·22 g.), and chloranil (1·23 g.) in benzene (200 c.c.) gave the blue quinone (1·22 g., 80%), m. p. 126—132°. Crystallisation from benzene–light petroleum gave the pure compound, m. p. and mixed m. p. 131—133°.

2 : 3 : 5-*Trichloro*-6-2′-*dimethylaminovinylbenzoquinone*.—The reaction was carried out between dimethylamine (1·44 g. of a 25% solution in water), acetaldehyde (0·18 g.), and chloranil (1 g.) in benzene (150 c.c.). The purple dimethylaminoquinone was separated from the blue quinone by chromatography. The blue *quinone* (0·58 g., 50%) formed needles, m. p. 143—144° (Found: C, 42·95; H, 2·85; N, 4·95; Cl, 38·1. $C_{10}H_8O_2NCl_3$ requires C, 42·8; H, 2·85; N, 5·0; Cl, 37·9%).

2 : 3 : 5-*Trichloro*-6-2′-*morpholinovinylbenzoquinone*.—Morpholine (3·6 g.), acetaldehyde (0·9 g.), and chloranil (4·9 g.) in benzene (250 c.c.) at 25° gave the blue *quinone* (4·27 g., 70%), m. p. 155—157° (needles from benzene) (Found: C, 44·85; H, 3·1. $C_{12}H_{10}O_3NCl_3$ requires C, 44·7; H, 3·1%).

2 : 3 : 5-*Trichloro*-6-2′-*piperidinovinylbenzoquinone*.—Piperidine (0·86 g.), acetaldehyde (0·25 g.), and chloranil (1·23 g.) in benzene (70 c.c.) at 25° gave a product which on chromatography afforded the quinone (0·41 g., 25%), m. p. and mixed m. p. 144—146°, whose infrared spectrum was identical with that of material prepared from 1-ethylpiperidine (preceding paper).

2 : 3 : 5-*Trichloro*-6-2′-*pyrrolidinovinylbenzoquinone*.—This was prepared from pyrrolidine (0·72 g.), acetaldehyde (0·25 g.), and chloranil (1·23 g.) in benzene (75 c.c.). Crystallisation from toluene–light petroleum (b. p. 60—80°) gave the *quinone* (0·85 g., 55%) as needles, m. p. 130—133° (decomp.) (Found: C, 47·1; H, 3·05. $C_{12}H_{10}O_2NCl_3$ requires C, 47·0; H, 3·3%).

2 : 3 : 5-*Trichloro*-6-2′-*hexamethyleneiminovinylbenzoquinone*.—Hexamethyleneimine (1·3 g.), acetaldehyde (0·3 g.), and chloranil (1·6 g.) in benzene (85 c.c.) led to the blue *quinone* (1·32 g., 55%), m. p. 119—121° (from benzene–light petroleum) (Found: C, 49·95; H, 4·1. $C_{14}H_{14}O_2NCl_3$ requires C, 50·25; H, 4·2%).

2 : 3 : 5-*Trichloro*-6-2′-(*methylanilino*)*vinylbenzoquinone*.—From the rate of production of blue colour the reaction with methylaniline was relatively slow, and the mixture of amine (1·1 g.), acetaldehyde (0·23 g.), and chloranil (1·23 g.) in benzene (50 c.c.) was kept at 25° for 2 hr. Chromatography separated much unchanged chloranil from the blue *quinone* (85 mg.), m. p. 161—163° (needles from toluene–light petroleum) (Found: C, 52·5; H, 3·8. $C_{15}H_{10}O_2NCl_3$ requires C, 52·55; H, 3·95%).

2 : 3 : 5-*Trichloro*-6-[2-*di*-(2-*hydroxyethyl*)*aminovinyl*]*benzoquinone*.—A different procedure was devised for the reaction of diethanolamine which is insoluble in benzene. The amine (2·1 g.) in ethanol (10 c.c.) was added to acetaldehyde (0·44 g.) and chloranil (2·46 g.) in dioxan at 10°. The mixture was allowed to warm to 20° during 45 min., then water (500 c.c.), benzene (100 c.c.), and ethyl acetate (100 c.c.) were added. The organic layer was dried, concentrated, and filtered through deactivated alumina (20 g.), elution of the blue quinone being completed with ethyl acetate. Evaporation under reduced pressure gave a product from which unchanged chloranil was extracted with cold benzene. The crude compound, m. p. 122—127°, was crystallised from slightly aqueous acetone, to give the blue *quinone* (0·18 g.) as needles, m. p. 132—135° (Found: C, 41·85; H, 3·75. $C_{12}H_{12}O_4NCl_3$ requires C, 41·7; H, 3·5%).

3 : 5-*Dichloro*-6-2′-*diethylaminovinyl*-2-*methoxybenzoquinone* (III).—This reaction was carried out in a solution in pure dioxan (12 c.c.) of 2 : 6-dichloro-3 : 5-dimethoxybenzoquinone (0·237 g.), diethylamine (0·15 g.), and acetaldehyde (0·045 g.). The product was isolated in benzene, chromatographed, and crystallised from toluene–light petroleum, to give the *quinone* (0·125 g., 40%), m. p. 119—121° (Found: C, 51·6; H, 4·75. $C_{13}H_{15}O_3NCl_2$ requires C, 51·3; H, 4·95%).

2 : 5-*Dichloro*-3 : 6-*bis*-2-*diethylaminovinylbenzoquinone* (II).—A mixture of diethylamine (1·45 g.), acetaldehyde (0·45 g.), and chloranil (1·23 g.) in benzene (500 c.c.) was kept at 22° for 1 hr. The purple solution was processed as for the monosubstituted quinone, crystallisation from toluene–light petroleum finally affording the purple *quinone* (0·99 g., 55%) as granular prisms, m. p. 127—133° (Found: C, 58·35; H, 6·55; N, 7·05; Cl, 19·35. $C_{18}H_{24}O_2N_2Cl_2$ requires C, 58·5; H, 6·5; N, 7·55; Cl, 19·1%).

[8] Farrar, Hamlet, Henbest, and Jones, *J.*, 1952, 2657.

2-Chloro-3-2'-dimethylaminovinyl-1 : 4-naphthaquinone (IV; R = Me).—This compound was prepared by the general procedure starting from dimethylamine (1·42 g. of a 25% solution in water), acetaldehyde (0·18 g.), and 2 : 3-dichloronaphthaquinone (0·8 g.) in benzene (150 c.c.). Elution of the crude product from alumina (100 g.) with benzene first gave the red 2-chloro-3-dimethylaminonaphthaquinone (0·11 g., 13%), m. p. 82—88° [pure, m. p. 88—89° (lit., 85°) (Found: C, 61·2; H, 4·2; N, 5·75. Calc. for $C_{12}H_{10}O_2NCl$: C, 61·1; H, 4·25; N, 5·95%)], and then the purple *quinone* (0·32 g., 35%). The pure product separated from slightly aqueous acetone as needles, m. p. 158—161° (Found: C, 64·6; H, 4·65. $C_{14}H_{12}O_2NCl$ requires C, 64·25; H, 4·6%).

2-Chloro-3-2'-diethylaminovinyl-1 : 4-naphthaquinone (IV; R = Et).—Diethylamine (1·36 g.), acetaldehyde (0·4 g.), and 2 : 3-dichloronaphthaquinone (1 g.) in benzene (50 c.c.) were stirred at 20° for 1 hr. Chromatography on alumina (200 g.) (elution with benzene) gave the red *2-chloro-3-diethylaminonaphthaquinone* (16 mg., 1·5%), m. p. 57—59° [pure compound had m. p. 58—60° (Found: C, 64·05; H, 5·3; N, 5·4. $C_{14}H_{14}O_2NCl$ requires C, 63·75; H, 5·35; N, 5·3%)], followed by the purple quinone (1·197 g., 94%), m. p. 81—88°. Crystallisation from toluene–light petroleum gave the pure compound, m. p. and mixed m. p. 92—95°.

2-Chloro-3-(4-diethylaminobuta-1 : 3-dienyl)-1 : 4-naphthaquinone (VI).—Freshly prepared 1-diethylaminobutadiene (0·9 g.) was added to a solution of 2 : 3-dichloro-1 : 4-naphthaquinone (0·545 g.) in benzene (25 c.c.) at 20°. After 3 min. the product was isolated as before. The *quinone* (0·6 g., 80%) formed blue needles, m. p. 128—130° (from toluene–light petroleum) (Found: C, 68·95; H, 5·75. $C_{18}H_{18}O_2NCl$ requires C, 69·2; H, 6·0%).

This compound was prepared in lower yield from diethylamine and crotonaldehyde. The pure aldehyde (0·14 g.) and the amine (0·28 g.) were added to the dichloroquinone (0·227 g.) in benzene (15 c.c.) containing sodium sulphate (0·2 g.). After the mixture had been stirred for 70 min. at 20° it was filtered, concentrated under reduced pressure, and placed on deactivated alumina (20 g.). Elution with benzene (10 c.c.) gave the red 2-chloro-3-diethylaminonaphthaquinone (83 mg., 33%), m. p. 55—58° (from light petroleum). Further elution with benzene (40 c.c.) gave the blue quinone (68 mg., 21%) which after crystallisation from toluene–light petroleum had m. p. 125—127°, undepressed on admixture with the compound prepared by the first method. The infrared spectra were also identical.

Chloranil and n-*Butylamine.*—A solution of the quinone (0·5 g.) and the amine (0·6 g., excess) in benzene (50 c.c.) was kept at 20° for 24 hr. The mixture was evaporated to dryness and the residue washed with water, to give 2 : 5-*bisbutylamino*-3 : 6-*dichlorobenzoquinone* (XIV) (0·50 g.), m. p. 201—202°. Crystallisation from dioxan–ethyl acetate gave pink plates, m. p. 202—203° (Found: C, 52·85; H, 6·3. $C_{14}H_{20}O_2N_2Cl_2$ requires C, 52·65; H, 6·3%). From a similar experiment with equimolar amounts of the quinone and amine, the same compound was obtained together with unchanged chloranil (separated chromatographically), and no mono-substituted compound could be detected.

2 : 5-*Dichloro*-3 : 6-*dimethoxy*-p-*benzoquinone and* n-*Butylamine.*—The amine (0·15 g., 2·05 mol.) was added to the quinone (0·237 g.) in benzene (15 c.c.) at 20°. The product began to separate as a pink precipitate within 1 min. After 30 min. the mixture was evaporated and the residue washed with water (these washings gave no precipitate with silver nitrate). Crystallisation from dioxan gave the foregoing quinone (XIV) (0·28 g., 88%), m. p. 202—203°. This compound was also obtained, with unchanged quinone (separated by chromatography), when equimolar quantities of amine and quinone were used.

2 : 5-*Dichlorobenzoquinone and* n-*Butylamine.*—The amine (0·15 g.) was added to the quinone (0·531 g.) in benzene (15 c.c.). The solution became red, and brown material was precipitated. After 15 min. the mixture was placed on a column of alumina (10 g.) which was developed with benzene. Evaporation of the eluate gave material which on crystallisation from dioxan gave the foregoing quinone (XIV) (70 mg., 22%), m. p. and mixed m. p. 201—202°.

2 : 6-*Dichlorobenzoquinone and* n-*Butylamine.*—The amine (0·45 g.) was added to a solution of the quinone (0·354 g.) in dioxan (10 c.c.). The solution became purple and then red. After 5 min. water was added until crystals (0·23 g., 81%), m. p. 169—171°, began to separate. Crystallisation from slightly aqueous dioxan gave 3-*chloro*-2 : 6-*bisbutylaminobenzoquinone* as red needles, m. p. 172—174° (Found: C, 58·85; H, 7·4; N, 9·95. $C_{14}H_{21}O_2N_2Cl$ requires C, 59·05; H, 7·45; N, 9·85%).

Chloranil and Morpholine.—The amine (0·5 g.) was added to chloranil (0·246 g.) in dioxan (10 c.c.). After 10 min. methanol (10 c.c.) and water (1 c.c.) were added and after a further

15 min. the (almost pure) product (0·247 g., 70%) was collected. 2 : 5-Dichloro-3 : 6-dimorpholinobenzoquinone (XVI) formed brownish plates, m. p. 200—203° (Found: C, 48·35; H, 4·7. Calc. for $C_{14}H_{16}O_4N_2Cl_2$: C, 48·45; H, 4·65%).

The amine (87 mg.) in acetone (5 c.c.) was added to chloranil (0·246 g.) in dioxan (5 c.c.) and acetone (5 c.c.). After 10 min. the purple solution was washed with dilute hydrochloric acid and the product (0·11 g., 74%) was separated from unchanged chloranil by chromatography on deactivated alumina (50 g.). 2 : 3 : 5-*Trichloro*-6-*morpholinobenzoquinone* had m. p. 157—158° (from toluene–light petroleum) (Found: C, 40·3; H, 2·6. $C_{10}H_8O_3NCl_3$ requires C, 40·5; H, 2·7%).

2 : 5-*Dimethoxybenzoquinone and* n-*Butylamine*.—The quinone (0·136 g.), amine (0·45 g.), and dioxan (20 c.c.) were heated on a steam-bath for 90 min. The quinone slowly dissolved and the solution became orange-red. It was cooled and water was added until the product (0·111 g., 65%), m. p. 162—165°, crystallised. Pure 2 : 5-bisbutylamino-*p*-benzoquinone (XX) separated from aqueous dioxan as vermilion plates, m. p. 164—165° (Found: C, 67·3; H, 8·9; N, 11·4. Calc. for $C_{14}H_{22}O_2N_2$: C, 67·2; H, 8·85; N, 11·2%).

2 : 6-*Dimethoxybenzoquinone and* n-*Butylamine*.—A mixture of the quinone (0·272 g.), the amine (0·44 g.), and dioxan (10 c.c.) was heated on a steam-bath for 6 hr. The solvent was removed under reduced pressure and the residue was extracted with benzene at 20°, leaving starting material (77 mg.). The benzene solution was placed on deactivated alumina (15 g.). A purple band was eluted with benzene which on evaporation gave a product (112 mg., 50%), m. p. 120—128°. Crystallisation from methanol gave pure 2 : 5-*bisbutylamino*-3-*methoxy*-*p*-*benzoquinone* (XXIV) as brownish needles with a purple sheen, m. p. 134—135° (Found: C, 64·0; H, 8·5; N, 10·4. $C_{15}H_{24}O_3N_2$ requires C, 64·25; H, 8·55; N, 10·0%).

2 : 6-*Dichloro*-3 : 5-*dimethoxybenzoquinone and* n-*Butylamine*.—The amine (0·292 g.) was added to a solution of the quinone (0·237 g.) in dioxan (10 c.c.). A permanganate colour developed which after a few minutes changed to mauve. After 1 hr. the solution was washed with dilute hydrochloric acid, then chromatographed over deactivated alumina. A mauve band was eluted with benzene. Crystallisation from benzene–light petroleum gave 2-*chloro*-3 : 6-*bisbutylamino*-5-*methoxybenzoquinone* (XXII) (0·21 g., 67%) as purple needles, m. p. 133—134° (Found: C, 57·1; H, 7·45; N, 9·15. $C_{15}H_{23}O_3N_2Cl$ requires C, 57·2; H, 7·35; N, 8·9%).

The quinone (0·237 g.) in dioxan (10 c.c.) was treated with *n*-butylamine (90 mg., 1·2 mol.). After 5 hr. at 20°, the purple solution was evaporated under reduced pressure, the residue being extracted with benzene–light petroleum (1 : 1) and placed on deactivated alumina (20 g.). Benzene eluted the purple band, the product from which was crystallised from ethanol to give the 2-*butylamino*-3 : 5-*dichloro*-6-*methoxybenzoquinone* (XXV) (0·155 g., 56%), m. p. 89—94°. The pure compound formed purple needles, m. p. 97—99° (Found: C, 47·2; H, 4·85; Cl, 25·7. $C_{11}H_{13}O_3NCl_2$ requires C, 47·5; H, 4·7; Cl, 25·5%).

Reactions of 2 : 3 : 5-*Trichloro*-6-2′-*morpholinovinylbenzoquinone with Amines*.—*n*-Butylamine (0·148 g., 4 mol.) in dioxan (3 c.c.) was added to a solution of the quinone (0·161 g.) in dioxan (12 c.c.). The solution rapidly became green and after 5 min. water was added to precipitate the product. Crystallisation from benzene gave 3-*butylamino*-6-2′-*butylaminovinyl*-2 : 5-*dichlorobenzoquinone* (XIII) (95 mg.), m. p. 161—162° (Found: C, 55·95; H, 6·35. $C_{16}H_{22}O_2N_2Cl_2$ requires C, 55·65; H, 6·4%).

Dimethylamine (0·36 g. of a 25% solution in water) in dioxan (2 c.c.) was added to a solution of the quinone (0·161 g.) in dioxan (12 c.c.). The solution rapidly became olive-green and after 5 min. water was added. The precipitate was dried and crystallised from benzene, to give 2 : 5-*dichloro*-3-*dimethylamino*-6-2′-*morpholinovinylbenzoquinone* (XII) (0·122 g.), m. p. 167—168° (decomp.) (Found: C, 51·1; H, 4·9. $C_{14}H_{16}O_3N_2Cl_2$ requires C, 50·75; H, 4·85%).

Competitive Reaction of the Chloranils with n-*Butylamine*.—The amine (73 mg.) in benzene (1 c.c.) was added to a solution of *o*-chloranil (0·123 g.) and *p*-chloranil (0·123 g.) in benzene (20 c.c.). The mixture was kept for 24 hr. at 20°. Chromatography gave unchanged *p*-chloranil (0·11 g., 89%) but no *o*-compound.

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