313. *Reactions Between Quinones and Unsaturated Amines. Part II.*[1] *The Detection of* N-*Alkylvinylamines in Equilibria with Ethylidene-amines.*

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The less stable vinylamines (CH$_2$=CH·NHR) can be detected in admixture with their tautomers (CH$_3$·CH=NR) by reaction with 2,3-dichloronaphthaquinone which produces purple 2-chloro-3-2'-alkylaminovinylnaphthaquinones (IV).

QUINONES with halogen substituents in the quinone ring react rapidly with *NN*-dialkylvinylamines (generated *in situ* from acetaldehyde and secondary amines), to give dialkylaminovinylquinones in high yield.[1] Thus the purple quinone (II) is produced in 90% yield from 2,3-dichloronaphthaquinone (I), acetaldehyde, and diethylamine in benzene at 20°.

N-Alkylvinylamines (CH$_2$=CH·NHR) should react with halogenated quinones in a similar way, giving monoalkylaminovinylquinones. Infrared and other evidence indicates that *N*-alkylvinylamines (in the absence of groups conferring stability by resonance) exist
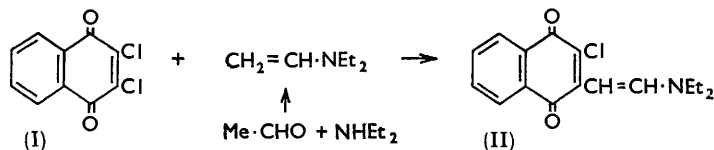
preferentially as *N*-ethylideneamines.[2,3] In agreement, each of the ethylidene compounds (IIIA; R = Bu^n and Et) used in the present study gave a strong C=N stretching band at 1670 cm.$^{-1}$ and only weak NH absorption in the 3300 cm.$^{-1}$ region. However, there is some infrared evidence[4] for the presence of a small proportion of the vinylamine tautomer in *N*-cyclohexylidenecyclohexylamine, and the slow racemisation of the condensation product from primary amines and (+)-2-methylbutanal indicates[5] the existence of the equilibrium: EtMeCH·CH=NR $\rightleftharpoons$ EtMeC=CH·NHR. Similar equilibrium between the tautomeric forms of ethylidene-amines (CH$_3$·CH=NR $\rightleftharpoons$ CH$_2$=CH·NHR) should lead, in the presence of a reactive quinone, to complete condensation of the ethylidene-amine in its vinylamine form. This was tested by adding *N*-ethylidenebutylamine (IIIA; R = Bu^n) to the 2,3-dichloro-quinone (I) in benzene. The solution at 20° slowly became blue-violet: chromatography then gave, in order of elution, the red butylaminoquinone (V; R = Bu^n),

[1] The paper by Buckley, Henbest, and Slade, *J.*, 1957, 4891, is regarded as Part I.
[2] Witkop, *J. Amer. Chem. Soc.*, 1956, **78**, 2873.
[3] Burckhalter and Short, *J. Org. Chem.*, 1958, **23**, 1278.
[4] Bergmann, Zimkin, and Pinchas, *Rec. Trav. chim.*, 1952, **71**, 186.
[5] Wegler and Ruzicka, *Ber.*, 1935, **68**, 1059.

an unidentified blue quinone, and the expected purple butylaminovinylquinone (IV; R = Bu^n). The structure of the last compound was confirmed by its infrared spectrum (NH band present) and by the close similarity of its ultraviolet and visible absorption to those of the dialkylaminovinyl series (cf. II).
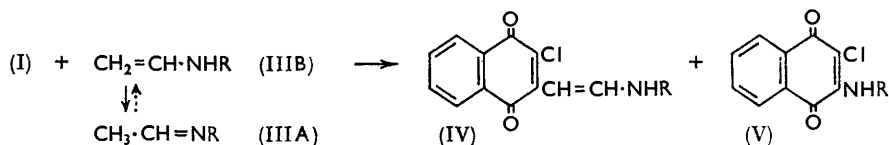
The formation of the red quinone (V; R = Bu^n) may be connected with that of the blue quinone. Analysis of the latter gave the formula $C_{26}H_{33}ClN_2O_2$, corresponding to a product formed from one molecule of the dichloroquinone (I) and four molecules of ethylidenebutylamine with loss of two molecules of butylamine and one molecule of hydrogen chloride.

Similar results were obtained when using ethylidene-ethylamine and the dichloro-quinone (I). The purple ethylaminovinylquinone (IV; R = Et) was obtained in some-what lower yield than its butyl analogue; it was accompanied by an approximately equal amount of the red ethylaminoquinone (V; R = Et) and a smaller amount of a blue quinone (not obtained pure).

The initial prototropic rearrangement, occurring in the conversion of either ethylidene-amine into its tautomeric vinylamine, should be facilitated by hydroxylic solvents that can act as proton sources. A spectrophotometric study of the reaction between the dichloro-quinone (I) and *N*-ethylidenebutylamine showed that formation of the purple quinone (IV; R = Bu^n) occurred much more rapidly and in better yield (45%) in 1 : 1 benzene–ethanol than in benzene alone (21%); conversely, the yield of the unknown blue quinone fell to 7% (from 27% in benzene alone).

EXPERIMENTAL

M. p.s were determined on a Kofler hot stage. Alumina deactivated with dilute acetic acid [6] was used for chromatography. The infrared absorptions (in KBr discs) of compounds were consistent with the structures given. Light petroleum refers to the fraction (b. p. 40—60°) unless stated otherwise.

Reaction between 2,3-Dichloronaphthaquinone (I) *and N-Ethylidenebutylamine.*—(a) *In benzene.* Freshly prepared *N*-ethylidenebutylamine [7] (3·96 g., 0·04 mole) was added to the quinone (2·27 g., 0·01 mole) dissolved in dry " AnalaR " benzene (120 c.c.). The mixture was kept at 20° for 4·5 hr., amine hydrochloride was removed, and the filtrate adsorbed on deactivated alumina (300 g.). Elution with benzene (250 c.c.) gave a red solid (0·35 g.), identified as 2-butylamino-3-chloronaphthaquinone (V; R = Bu^n) (see below), m. p. and mixed m. p. 113—114° (from light petroleum, b. p. 60—80°). Further elution with benzene afforded material (1·46 g.) that gave, after several crystallisations from light petroleum (b. p. 60—80°), a blue *quinone*, m. p. 118—121° (Found: C, 70·8; H, 7·35; N, 6·3; Cl, 8·65. $C_{26}H_{33}ClN_2O_2$ requires C, 70·8; H, 7·55; N, 6·35; Cl, 8·05%), $\lambda_{max.}$ (in dioxan) 2460, 2770, 3710, and 6350 Å (ε 13,200, 6500, 24,000, and 2000 respectively). Further elution gave the purple 2-2'-*butylaminovinyl-3-chloronaphthaquinone* (IV; R = Bu^n) (crude, 0·75 g.), m. p. 119—120° [from 1 : 3 toluene–light petroleum (b. p. 40—60°)] (Found, after heating at 55°/0·05 mm. to remove toluene of solvation: C, 66·2; H, 5·5. $C_{16}H_{16}ClNO_2$ requires C, 66·35; H, 5·55%), $\lambda_{max.}$ (in dioxan) 2380, 3140, and 5460 Å (ε 10,200, 24,100, and 9870 respectively). An NH band (in KBr) was present at 2280 cm.$^{-1}$.

(b) *In ethanol.* The reaction was carried between the quinone (0·227 g., 0·001 mole) and *N*-ethylidenebutylamine (0·396 g., 0·004 mole) in dry ethanol (200 c.c.) at 20° for 60 hr. The mixture was filtered, the filtrate evaporated, and the residue chromatographed on deactivated

[6] Farrar, Hamlet, Henbest, and Jones, *J.*, 1952, 2657.
[7] Campbell, Sommers, and Campbell, *J. Amer. Chem. Soc.*, 1944, **66**, 82.

alumina (100 g.). Separation as before gave the butylaminoquinone (V; R = Bu^n) (66 mg.) and the purple quinone (IV; R = Bu^n) (50 mg.) as the main isolable products.

(c) *In benzene–t-butyl alcohol.* The quinone (0·227 g., 0·001 mole) and *N*-ethylidenebutyl-amine (0·395 g., 0·004 mole) were kept in benzene (25 c.c.) and t-butyl alcohol (25 c.c.) at 20° for 60 hr. More benzene (100 c.c.) was added and the alcohol was washed out with water. The benzene solution was chromatographed as before, to give the red quinone (V; R = Bu^n) (64 mg.) and the purple quinone (IV; R = Bu^n) (81 mg.) as the main isolable products.

Spectrophotometric Examination of the Reaction.—*N*-Ethylidenebutylamine (0·396 g.) was added to the quinone (0·227 g.) in a purified solvent at 25°. Aliquot parts (1 c.c.) were removed periodically, diluted ten-fold, and examined spectrophotometrically (1 cm. cell) at the wave-length of maximal absorption of the purple quinone (IV; R = Bu^n) (5410 Å in benzene; 5750 Å in benzene–ethanol, 1 : 1), and at the wavelength of maximal absorption of the unknown blue quinone (6380 Å in benzene; 6750 Å in benzene–ethanol, 1 : 1). The results tabulated show that the purple quinone is formed more rapidly when ethanol is present.

The yields of purple quinone (IV; R = Bu^n) and blue quinone were computed from the final values of the extinction coefficients at the long-wave maxima, allowances being made for the absorption of the other compound [the absorption of the red quinone (V) was negligible at these wavelengths]. The yields of purple quinone were 21% and 45% (respectively in benzene

Time (hr.)	0	0·5	1	2
In C$_6$H$_6$: D at 5410 Å	0	0·025	0·046	0·137
In C$_6$H$_6$–EtOH: D at 5750 Å	0	0·382	0·725	0·980

and benzene–ethanol, 1 : 1) and the yields of blue quinone 27% and 7% (respectively in benzene and benzene–ethanol, 1 : 1).

Reaction between 2,3-Dichloronaphthaquinone (I) *and* N-*Ethylidene-ethylamine.*—A solution of the quinone (2·27 g., 0·01 mole) and *N*-ethylidene-ethylamine (2·84 g., 0·04 mole) in ethanol (2 l.) was kept at 20° for 124 hr. and then evaporated under reduced pressure. The residue was extracted with benzene, the extract being adsorbed on deactivated alumina (300 g.). Elution with benzene (1 l.) gave 2-chloro-3-ethylaminonaphthaquinone (0·49 g.), m. p. and mixed m. p. 131—132° (see below), followed by blue material. A purple fraction was finally eluted with benzene (2·5 l.); this yielded, after several crystallisations from 1 : 3 toluene–light petroleum (b. p. 40—60°), *2-chloro-3-ethylaminovinylnaphthaquinone* (IV; R = Et) (0·31 g.), m. p. 154—155° (Found: C, 64·45; H, 4·6. C$_{14}$H$_{12}$ClNO$_2$ requires C, 64·25; H, 4·6%); $\lambda_{max.}$ (in dioxan), 2340, 3140, and 5440 Å (ε 8900, 26,400, and 10,900 respectively).

2-Butylamino-3-chloronaphthaquinone (V; R = Bu^n).—A solution of 2,3-dichloronaphtha-quinone (0·454 g.) and butylamine (0·30 g.) in benzene (20 c.c.) was kept at 20° for 48 hr., then filtered through deactivated alumina (50 g.). Removal of solvent gave material (0·504 g., 96%), m. p. 111—112°, that on crystallisation from light petroleum (b. p. 60—80°) gave the *butylaminoquinone* as red needles, m. p. 112—114° (Found: C, 63·8; H, 5·4. C$_{14}$H$_{14}$ClNO$_2$ requires C, 63·75; H, 5·35%).

2-Chloro-3-ethylaminonaphthaquinone (V; R = Et).—This was prepared as in the previous experiment from the dichloroquinone (0·454 g.) and ethylamine (0·2 g.) in benzene (25 c.c.). The quinone (95% yield) crystallised from benzene–light petroleum (b. p. 60—80°) as red needles, m. p. 133—134° (Found: C, 61·7; H, 4·25; N, 5·75. Calc. for C$_{12}$H$_{10}$ClNO$_2$: C, 61·1; H, 4·25; N, 5·95%). This m. p. was consistently obtained although lower values [8,9] (110° and 115° respectively) have been given previously for the compound.

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[8] Plagemann, *Ber.*, 1882, **15**, 484.
[9] Kiprianov and Stetsenko, *Ukrain. khim. Zhur.*, 1953, **19**, 508; *Chem. Abs.*, 1955, **49**, 8263.