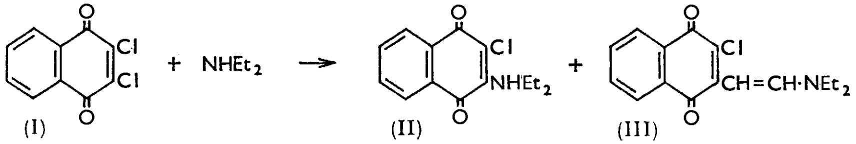
# **314.** *Amine Oxidation. Part V.* Dehydrogenation of Diethylamine in the Presence of 2,3-Dichloronaphthaquinone.*

By H. B. Henbest and P. Slade.

The dehydrogenation of diethylamine (by benzoyl peroxide or by a quinone) is complicated by reaction of the initial product, ethylidene-ethylamine, $CH_3{\cdot}CH{=}NEt$, with unchanged diethylamine which gives ethylamine and the tertiary enamine, $CH_2{=}CH{\cdot}NEt_2$. The last two compounds were detected in reaction mixtures as their coloured condensation products with 2,3-dichloronaphthaquinone.

Dehydrogenation of diethylamine may be expected to give ethylidene-ethylamine, $CH_3{\cdot}CH{=}NEt$, by analogy with, for example, the dehydrogenation of benzylaniline (by diphenylpicrylhydrazyl) to benzylideneaniline,[1] of pyrrolidine (*via* 1-chloropyrrolidine) to $\Delta^1$-pyrroline,[2] and of various secondary amines by silver persulphate.[3] It was decided to study the dehydrogenation of the simple secondary amine, diethylamine, in the presence of 2,3-dichloronaphthaquinone as the experiments described in the preceding paper demonstrated that the expected dehydrogenation product, ethylidene-ethylamine, reacts (in its tautomeric form) with this chloro-quinone to give a purple condensation product (IV). However, more complicated mixtures were generally obtained, owing to reaction of the first formed ethylidene-ethylamine with unchanged diethylamine.



*Reactions of Secondary Amines with Halogenated Quinones.*—The usual reaction involves replacement of halogen by a dialkylamino-group. In this way, 2,3-dichloronaphthaquinone (I) (1 mol.) and diethylamine (2 mols.) in benzene gave the red diethylaminoquinone (II) in 73% yield. Chromatography of the remainder of the product showed that *ca.* 8% of the diethylaminovinylquinone[4] (III) was also formed. This showed that vinyldiethylamine, $CH_2{=}CH{\cdot}NEt_2$, must be formed, and to explain it, it was postulated that part of the diethylamine is dehydrogenated by the dichloroquinone (I) to *N*-ethylidene-ethylamine, which can then generate diethylvinylamine by reaction with another molecule of diethylamine:

$$Me{\cdot}CH{=}NEt + Et_2NH \rightleftharpoons Me{\cdot}CH(NEt_2){\cdot}NHEt \rightleftharpoons CH_2{=}CH{\cdot}NEt_2 + NH_2Et$$

According to this scheme, the yield of the diethylaminovinylquinone (III) would be raised (at the expense of the ordinary replacement product, II) if *N*-ethylidene-ethylamine were added at the beginning of the reaction between the dichloro-quinone (I) and diethylamine. This was confirmed, a 31% yield of the diethylaminovinylquinone (III) being obtained from a reaction between 1 mol. each of the quinone (I), diethylamine, and *N*-ethylidene-ethylamine. In accord with the equilibrium between the amines postulated above, it was also possible to detect the formation of ethylamine, its reaction product (V) from the chloro-quinone (I) being isolated. The fourth product obtained was the ethylaminovinylquinone (IV), formed from ethylidene-ethylamine and the initial quinone (cf. preceding paper).

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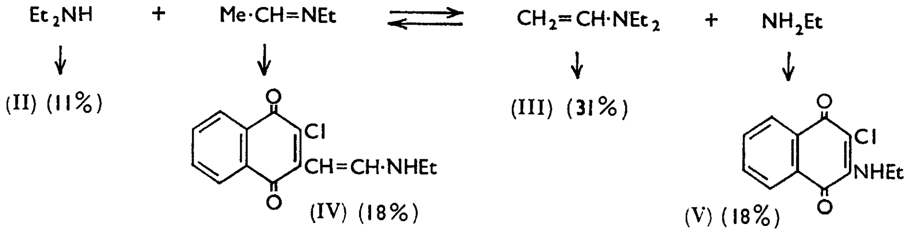
* Part IV, *J.*, 1957, 4905.

[1] Braude, Brook, and Linstead, *J.*, 1954, 3574.

[2] Fuhlhage and Vander Werf, *J. Amer. Chem. Soc.*, 1958, **80**, 6249.

[3] Bacon, Munro, and Stewart, unpublished work in these laboratories.

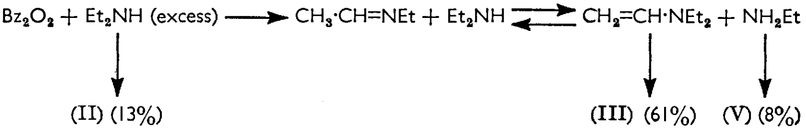
[4] Buckley, Henbest, and Slade, *J.*, 1957, 4891.



*Reactions of Secondary Amines with Benzoyl Peroxide.*—Gambarjan [5] has shown that dialkylamines with benzoyl peroxide readily give *NN*-dialkyl-*O*-benzoylhydroxylamines (*e.g.*, VI), often in high yields:

$$Et_2NH + Bz_2O_2 \longrightarrow Et_2N{\cdot}OBz\ (VI) + BzOH$$

The reaction between diethylamine (6 mols.) and benzoyl peroxide (2 mols.) in benzene has now been studied in the presence of 2,3-dichloronaphthaquinone (I) (1 mol.) with the following results:



$$\begin{tikzcd}
Bz_2O_2 + Et_2NH\ (excess) \arrow[r] \arrow[d] & CH_3{\cdot}CH{=}NEt + Et_2NH \arrow[r, shift left] & CH_2{=}CH{\cdot}NEt_2 \arrow[l, shift left] \arrow[d] & + NH_2Et \arrow[d] \\
(II)\ (13\%) & & (III)\ (61\%) & (V)\ (8\%)
\end{tikzcd}$$

The experiment indicates that the peroxide dehydrogenates the diethylamine [more quickly than the latter reacts with the dichloroquinone; cf. low yield of replacement product (II)], giving a product ($CH_3{\cdot}CH{=}NEt$) that reacts as before with diethylamine to give the amine precursors of the substituted quinones (III) and (V). The relatively low yield of the ethylaminoquinone (V) may be due to loss of ethylamine by reaction with unchanged peroxide. The failure to detect the condensation product (IV) that could be expected from the postulated intermediate production of ethylidene-ethylamine may be due to its more rapid reaction with the excess of diethylamine present.

*O*-Benzoyl-*NN*-diethylhydroxylamine (VI) is a possible intermediate in this reaction between diethylamine, benzoyl peroxide, and 2,3-dichloronaphthaquinone, for it could lose benzoic acid by a base-catalysed elimination to give ethylidene-ethylamine and thence the final products. However, addition of the hydroxylamine compound (VI) to a mixture of diethylamine and the dichloroquinone caused no appreciable difference to the reaction normally taking place between these two compounds, the diethylamino- and the diethylaminovinyl-quinones (II and III) being obtained in yields similar to those obtained in the first reaction described in this paper. It appears, therefore, that the presence of 2,3-dichloronaphthaquinone in the reaction between diethylamine and benzoyl peroxide causes a diversion from the path that normally leads to *O*-benzoyldiethylhydroxylamine.

## EXPERIMENTAL

General directions are given in the preceding paper. Yields of quinone products are based on the dichloronaphthaquinone that underwent reaction.

*Oxidation of Diethylamine by 2,3-Dichloronaphthaquinone.*—(a) *In benzene.* The dichloroquinone (0·227 g., $10^{-3}$ mole) and diethylamine (0·146 g., $2 \times 10^{-3}$ mole) were mixed in benzene (20 c.c.) in the presence of anhydrous magnesium sulphate (1 g.). After being kept for 7 days at 20°, the solution was filtered and chromatographed on deactivated alumina (100 g.). Elution with benzene–light petroleum (1 : 1) (250 c.c.) yielded a red solid (0·193 g., 73%), identified, after crystallisation from benzene–light petroleum, as 2-chloro-3-diethylaminonaphthaquinone (II), m. p. and mixed m. p. 57—60°. Further elution with benzene (350 c.c.) gave a mauve solid (25 mg., 8%), m. p. 89—93°, shown, by the identity of its infrared spectrum, to be 2-chloro-3-diethylaminovinylnaphthaquinone (III).

(b) *In ethanol.* The reaction was repeated in ethanol (200 c.c.). After 7 days, the solution

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[5] Gambarjan, *Ber.*, 1925, **58**, 1775; Gambarjan and Cialtician, *Ber.*, 1927, **60**, 390.

was evaporated under reduced pressure to dryness and the residue dissolved in benzene (20 c.c.). Chromatography gave 2-chloro-3-diethylaminonaphthaquinone (0·184 g., 70%) and 2-chloro-3-diethylaminovinylnaphthaquinone (35 mg., 12%).

*Reaction between* 2,3-*Dichloronaphthaquinone, Diethylamine, and Ethylidene-ethylamine.*—Ethylidene-ethylamine (0·142 g., 2 × $10^{-3}$ mole) and diethylamine (0·146 g., 2 × $10^{-3}$ mole) were added to 2,3-dichloronaphthaquinone (0·454 g., 2 × $10^{-3}$ mole) in dry benzene (50 c.c.). After 24 hr. at 20°, the mixture was filtered to leave diethylamine hydrochloride, identified by its infrared spectrum. The filtrate was chromatographed on deactivated alumina (250 g.). Elution with benzene–light petroleum (1 : 1) (500 c.c.) yielded a mixed fraction (see below). Elution with benzene (500 c.c.) gave 2-chloro-3-diethylaminovinylnaphthaquinone (III) (0·128 g., 31%), m. p. 88—92°, and with more benzene (500 c.c.) gave 2-chloro-3-ethylaminovinylnaphthaquinone (IV) (67 mg., 18%), m. p. 145—153°. These two products were further identified by their infrared spectra.

The mixed fraction was rechromatographed on deactivated alumina (100 g.). Elution with light petroleum (400 c.c.) yielded dichloronaphthaquinone (0·126 g.), m. p. and mixed m. p. 190—194°; then benzene–light petroleum (1 : 1) (200 c.c.) gave 2-chloro-3-diethylaminonaphthaquinone (II) (40 mg., 11%), m. p. 55—59°. Finally elution with benzene (200 c.c.) gave 2-chloro-3-ethylaminonaphthaquinone (V) (49 mg., 14%), m. p. 128—130°. The last two products were further identified by their infrared spectra.

*Oxidation of Diethylamine by Benzoyl Peroxide in the Presence of* 2,3-*Dichloronaphthaquinone.*—The dichloroquinone (0·227 g., $10^{-3}$ mole) was dissolved in dry benzene (50 c.c.), and recrystallised benzoyl peroxide (0·484 g., 2 × $10^{-3}$ mole) and diethylamine (0·438 g., 6 × $10^{-3}$ mole) were added. After 22 hr. at 20°, the mixture was filtered and chromatographed on deactivated alumina (200 g.). (The white crystals filtered off were identified as diethylamine hydrochloride by infrared spectroscopy.) Elution with benzene–light petroleum (1 : 1) (400 c.c.) gave a mixed fraction, and elution with benzene (500 c.c.) gave 2-chloro-3-diethylaminovinylnaphthaquinone (III) (0·102 g., 61%), identified by its infrared spectrum. Rechromatography of the mixed fraction on deactivated alumina (100 g.) afforded unchanged dichloroquinone (95 mg.), 2-chloro-3-diethylaminonaphthaquinone (II) (20 mg., 13%), m. p. 50—55°, and 2-chloro-3-ethylaminonaphthaquinone (V) (12 mg., 8%), m. p. 120—125°, the last two compounds being further identified by infrared spectroscopy.

*Attempted Reaction Between* O-*Benzoyl*-NN-*diethylhydroxylamine, Diethylamine, and* 2,3-*Dichloronaphthaquinone.*—A solution of 2,3-dichloronaphthaquinone (0·454 g., 2 × $10^{-3}$ mole), *O*-benzoyl-*NN*-diethylhydroxylamine (0·772 g., 4 × $10^{-3}$ mole), and diethylamine (0·584 g., 8 × $10^{-3}$ mole) in benzene (50 c.c.) was kept at 20° for 7 days. Filtration and chromatography in the usual way gave 2-chloro-3-diethylaminonaphthaquinone (II) (0·379 g., 72%) and 2-chloro-3-diethylaminovinylnaphthaquinone (III) (48 mg., 8%).

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THE QUEEN'S UNIVERSITY OF BELFAST.

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