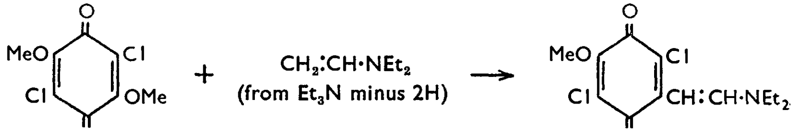
983. *Amine Oxidation. Part III.*[1] *A Test Reaction for the Dehydrogenation of Triethylamine. The Reactions of Some Tertiary Amines with Benzoyl Peroxide.*

By D. Buckley, Sonia Dunstan, and H. B. Henbest.

Dehydrogenation of triethylamine (or other suitable tertiary amines) by an oxidising agent can be detected by the formation of a blue quinone if the reaction is carried out in the presence of a dichlorodimethoxy-*p*-benzoquinone. One of the effective reagents is benzoyl peroxide, and some of its reactions with tertiary amines are discussed.

When triethylamine is added to a dilute (yellow) solution of 2 : 5-dichloro-3 : 6-dimethoxybenzoquinone (I) in benzene the colour deepens somewhat owing to complex formation, but in the absence of strong light the solution does not become blue, *i.e.*, a dialkylaminovinyl-quinone, which could be formed by dehydrogenation of the amine followed by coupling of the resulting enamine with the starting quinone,[1] is not produced. However, on addition of some benzoyl peroxide a blue colour developed rapidly, owing to formation of the diethylaminovinyl-quinone (II). The conclusion follows that benzoyl peroxide is effective in dehydrogenating triethylamine to diethylvinylamine, which then displaces a methoxyl group from the quinone (I) to give the blue compound (II): this displacement also takes place with other nucleophils, *e.g.*, *n*-butylamine.[2] Violently exothermic reactions often take place on addition of benzoyl peroxide to tertiary amines,[3] but controlled reactions can be carried out in more dilute solution and secondary amines and carbonyl compounds can be obtained after hydrolysis [4, 5] (cf. below). The present reaction, in the presence of the quinone (I), constitutes the first demonstration that an enamine can be formed from a tertiary amine and the peroxide.



(I) (II)

By using development of a blue colour from the quinone (I) and triethylamine as a test for enamine formation from the tertiary amine, it has been shown that *N*-bromosuccinimide and 3 : 3′ : 5 : 5′-tetrachlorodiphenoquinone also dehydrogenate the amine in dilute benzene solution. Manganese dioxide gave a negative reaction, but the principle has been used to detect the occurrence of dehydrogenation on treatment of diethylaniline with the dioxide in the presence of chloranil (which alone does not readily dehydrogenate diethylaniline), and a blue quinone was isolated.[6]

The test reaction with *N*-bromosuccinimide was exceptional in that the blue colour did not develop gradually but appeared suddenly after several minutes. Separate experiments showed that the blue quinone (II) was decolorised by *N*-bromosuccinimide in benzene solution, and thus the blue colour appears only when all of the bromo-imide has reacted (see also the following paper).

The observations that triethylamine is dehydrogenated by chloranil but not by *p*-benzoquinone[1] at room temperature are paralleled by the positive and negative result

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[1] Part II, Buckley, Dunstan, and Henbest, *J.*, 1957, 4880.

[2] Buckley, Henbest, and Slade, preceding paper.

[3] Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686; 1947, **69**, 2299; Horner and Schwenk, *Annalen*, 1950, **566**, 69.

[4] Paolini and Ribet, *Gazzetta*, 1932, **62**, 1041; Gambarjan and Kazarjan, *J. Gen. Chem.* (*U.S.S.R.*), 1933, **2**, 222.

[5] Horner and Kirmse, *Annalen*, 1955, **597**, 48.

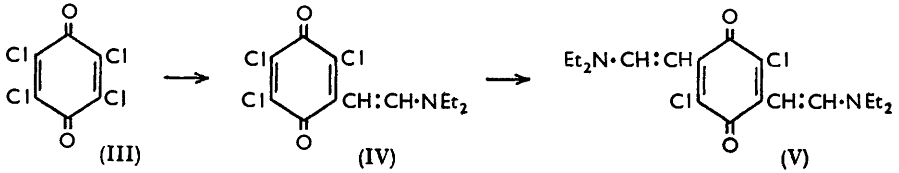
[6] Henbest and Thomas, *J.*, 1957, 3032.

given respectively in the above test reaction by the tetrachlorodiphenoquinone and by diphenoquinone. In the case of chloranil, dehydrogenation of the tertiary amine can be detected by the formation of a blue quinone without the addition of a second quinone such as (I). However the presence of the quinone (I) is essential for colour production from the tetrachlorodiphenoquinone as the latter quinone (in contrast to chloranil) is not substituted by the enamine to give a coloured product.

Reactions of Benzoyl Peroxide with Amines containing an $R_2N{\cdot}CH_2{\cdot}CH_2$ *Grouping.*—In the reaction of triethylamine (excess) with benzoyl peroxide in the presence of the quinone (I) the yield of blue quinone (II) was proportional to the amount of peroxide added up to a peroxide : quinone ratio of 1 : 1. A similar relation was found for the corresponding reaction in the presence of chloranil (III), allowance being made for the concurrent (slower) dehydrogenation caused by this quinone. The results are consistent with a dehydrogenation as follows:

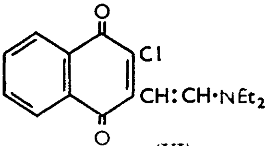
$$Et_3N + Bz_2O_2 \longrightarrow Et_2N{\cdot}CH{:}CH_2 + 2BzOH$$

The yields of blue compound from quinone (I) were consistently lower than those of the corresponding product from chloranil (III). This is probably due to the lower reactivity of the former quinone towards the nucleophilic enamine, the chances of the enamine undergoing alternative reactions such as polymerisation (encouraged by the presence of the peroxide) being increased. The quinone (I) also reacted more slowly than chloranil with the simpler nucleophilic reagent, diethylamine.

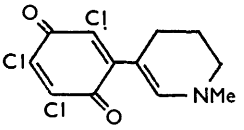


(III) (IV) (V)

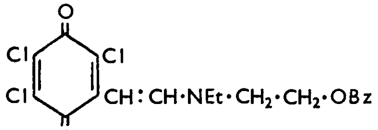
When increasing amounts of benzoyl peroxide were added to chloranil and an excess of triethylamine in benzene solution, the blue colour initially formed was replaced by a purple colour due to the formation of the bisdiethylaminovinylquinone (V). The pure compound was best obtained by this method starting from the blue quinone (IV); it was identical with the product formed by the acetaldehyde–diethylamine method.[2]



(VI)



(VII)



(VIII)

The slow dehydrogenation of triethylamine by 2-chloronaphtha-1 : 4-quinone and the formation of the purple quinone (VI) in low yield has been described.[1] By using benzoyl peroxide as the dehydrogenating reagent a much better yield of the same quinone (VI) was obtained more quickly. From the point of view of the production of dialkylamino-vinyl-quinones, generation of the necessary enamine by the amine–peroxide reaction is of most value where the usually more convenient aldehyde–secondary amine method [2] is not easily applied: synthesis of the blue quinone (VII) by dehydrogenating 1-methylpiperidine with benzoyl peroxide in the presence of chloranil provides such an example, the amino-aldehyde necessary for the alternative method of synthesis not being easily available, and chloranil itself not readily introducing a double bond into a piperidine ring.[1]

Diethylaminoethanol with benzoyl peroxide and chloranil gave the blue quinone (IV) in 10% yield, corresponding to dehydration of the initial amine. Its benzoate gave, in contrast, the blue quinone (VIII) in 10% yield.

Reactions of Benzoyl Peroxide with Amines of the $Me_2N{\cdot}CH_2Ar$ *Type.*—These amines cannot form enamines on dehydrogenation, but hydrolysis of an intermediate,

$Me_2N\cdot CHAr\cdot OBz$, should give a carbonyl compound and a secondary amine. Previous work[4, 5] on the tertiary amine–benzoyl peroxide reaction has been concerned with this overall process, which can take place in principle with all amines containing an $>N\cdot CH<$ grouping.

In the present study the oxidation of some unsymmetrical amines of the benzyldimethylamine type was examined, attention being directed towards the amounts of aromatic aldehydes produced. The yields show that there is in each case some preference for oxidation to be directed into the benzyl grouping, and that relatively small differences in yield result from variation of a *para*-substituent.

Comments.—To aid a search for intermediates the infrared absorptions of mixtures of amine and benzoyl peroxide were determined in the 1900—1600 cm.$^{-1}$ region. With one exception, diminution of the twin peaks given by benzoyl peroxide at 1785 and 1762 cm.$^{-1}$ was accompanied by development of a broader peak near 1705 cm.$^{-1}$. The new peak may be attributed to intermediates of structure, $R_2N\cdot CHR'\cdot OBz$, and/or to benzoic acid, separate experiments showing that the presence of a tertiary amine did not appreciably alter the position of the carbonyl peak of this acid.

Rates were compared by determining the time in each reaction for the intensities of the diminishing 1762 cm.$^{-1}$ peroxide peak and the rising 1705 cm.$^{-1}$ peak to become equal. Thus the reaction velocity was found to depend on the steric accessibility of the nitrogen atom in the amine. In triethylenediamine, $N[CH_2\cdot CH_2]_3N$, the nitrogen atoms are very exposed but intermediates of the type $[R_2N{:}CHR']^+$ should be formed only with difficulty or not at all (Bredt's rule): in line with this, reaction was very rapid—under the standard conditions the 1762 cm.$^{-1}$ peak disappeared before measurements could be taken—and a peak developed at 1780 as well as at 1705 cm.$^{-1}$. The peak at 1780 cm.$^{-1}$ may possibly be attributed to the cation, $\{N[CH_2\cdot CH_2]_3N\cdot Bz\}^+$, a type of structure not likely to be stable in simpler amines where loss of benzoic acid can take place without difficulty. The 1780 cm.$^{-1}$ peak diminished gradually: the final products have not been investigated.

These results are consistent with a heterolytic mechanism involving the displacement of benzoate anion from the peroxide by a nucleophilic trialkylamine molecule. An analogy may be drawn with the reaction of benzoyl peroxide with the strongly nucleophilic alkoxides.[7]

$$\begin{tikzcd}
R_2N\cdot CH_2R' + Bz_2O_2 \arrow[r] & {[R_2N(CH_2R')\cdot OBz]^+ + BzO^-} \arrow[d, shift left, "-BzOH"] & \\
\text{Enamine}^{*} & {[R_2N{:}CHR']^+} \arrow[l, "-H^+"'] \arrow[r, "H_2O"] \arrow[u, shift left] & R_2NH + R'\cdot CHO
\end{tikzcd}$$

* If R′ = Me or another group containing CH.

It has been suggested before that the reactions of dialkylanilines proceed by such a heterolytic mechanism,[8] but on the other hand formation of radical intermediates in tertiary amine–benzoyl peroxide reactions has been urged.[5] Further discussion is deferred until more evidence is available.

EXPERIMENTAL

Solvents and reagents were purified: it was particularly important to remove acetal impurities from dioxan.

Test Reaction.—A few mg. of dehydrogenating reagent were added to 5 c.c. of a freshly prepared benzene solution of 2 : 5-dichloro-3 : 6-dimethoxy-*p*-benzoquinone (0·04M) and triethylamine (0·08M). Development of a blue colour within 30 min. in subdued light indicated dehydrogenation. Positive tests were given by benzoyl peroxide, 3 : 3′ : 5 : 5′-tetrachlorodiphenoquinone and *N*-bromosuccinimide: negative tests by manganese dioxide, iodine, di-*tert.*-butyl peroxide, and diphenoquinone.

Dehydrogenation of Triethylamine.—(a) *In the presence of* 2 : 5-*dichloro*-3 : 6-*dimethoxy*-p-*benzoquinone.* The amine (0·8 g.) was added to a solution of the quinone (0·41 g.) and benzoyl

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[7] Doering and Greenbaum, quoted by Greenbaum, Denny, and Hoffmann, *J. Amer. Chem. Soc.*, 1956, **78**, 2563.

[8] Imoto and Takemoto, *J. Polymer Sci.*, 1956, **19**, 579.

peroxide (0·484 g.) in benzene (25 c.c.). After 1·5 hr. the blue solution was filtered from triethylamine hydrochloride (90 mg.), m. p. 254—255° (sealed tube) after crystallisation from *iso*propyl alcohol, and washed with dilute hydrochloric acid and dilute aqueous sodium hydroxide. Filtration of the blue solution through deactivated alumina (10 g.) followed by crystallisation of the product from light petroleum (b. p. 60—80°) gave the blue 2 : 5-*dichloro*-3-2′-*diethylaminovinyl*-6-*methoxybenzoquinone* (II) (0·11 g.) as needles, m. p. 109—110° (Found: C, 51·15; H, 4·95. $C_{13}H_{15}O_3NCl_2$ requires C, 51·3; H, 4·95%).

(b) *In the presence of* 2-*chloronaphthaquinone.* Benzoyl peroxide (1·22 g.) in benzene (100 c.c.) was added to a solution of the quinone (0·96 g.) and triethylamine (1·5 g.) in benzene (100 c.c.). After 1 hr. at 20°, the deep purple solution was washed with dilute sodium hydroxide solution until benzoic acid had been removed. The benzene solution was filtered through deactivated alumina (25 g.) and evaporated. The residue was dissolved in acetone and water was added to induce crystallisation. 2-Chloro-3-2′-diethylaminovinylnaphtha-1 : 4-quinone (0·35 g., 48%) had m. p. and mixed m. p. 95—99° and light absorption properties identical with those of the product made by alternative methods (two previous papers).

(c) *In the presence of the blue quinone* (IV). Benzoyl peroxide (0·73 g.) was added to a solution of the quinone (0·92 g.) and triethylamine (1·2 g.) in benzene (90 c.c.). After 3 hr. at 20°, the purple solution was worked up in the usual way, and the product chromatographed on deactivated alumina. Crystallisation from toluene–light petroleum gave the quinone (V) (0·537 g.), m. p. 129—130°. M. p. and light absorption comparisons confirmed its identity with the compound prepared as in the previous paper.

Dehydrogenation of 1-*Methylpiperidine.*—A solution of chloranil (3 g.), benzoyl peroxide (3 g.), and the amine (5 g.) in benzene (700 c.c.) was kept at 15° for 2·5 hr., then washed with N-sulphuric acid and 5% sodium hydroxide solution, dried, and evaporated under reduced pressure. Crystallisation from toluene–light petroleum gave the blue 2 : 3 : 6-*trichloro*-5-(1 : 4 : 5 : 6-*tetrahydro*-1-*methyl*-3-*pyridyl*)*benzoquinone* (VII) (0·45 g.), m. p. 105—107° (decomp.) (Found: C, 47·0; H, 3·4; N, 4·85. $C_{12}H_{10}O_2NCl_3$ requires C, 47·0; H, 3·3; N, 4·55%).

Dehydrogenation of 2-*Diethylaminoethyl Benzoate.*—The amino-ester (9·7 g.) was added to chloranil (4·91 g.) and benzoyl peroxide (4·84 g.) in benzene (700 c.c.) at 20°. The solution became green, then blue. The change in concentration of blue quinone was followed spectrophotometrically at 6300 Å and the reaction was shown to be complete within 40 hr. The solution was decanted from green tar, washed with 0·2N-sodium hydroxide, water, 0·2N-hydrochloric acid, and water and dried (Na_2SO_4). The product was chromatographed on deactivated alumina (100 g.). Elution with benzene–light petroleum (1 : 2) yielded unchanged chloranil, followed by the principal blue band. Crystallisation of this blue compound (0·9 g.) from toluene–light petroleum gave 2-[2-(N-2-*benzoyloxyethyl*-N-*ethylamino*)*vinyl*]-3 : 5 : 6-*trichlorobenzoquinone* (VIII), m. p. 135—136·5° (Found: C, 53·7; H, 4·0; N, 3·4. $C_{19}H_{16}O_4NCl_3$ requires C, 53·2; H, 3·75; N, 3·25%), with infrared bands (in Nujol) at 1710 (benzoate-carbonyl) and 1670 cm.$^{-1}$ (non-conjugated quinone-carbonyl).

From a similar reaction between 2-diethylaminoethanol (8 g.), chloranil (5 g.), and benzoyl peroxide (5 g.) in benzene at 20° for 18 hr. (reaction complete), the blue quinone (IV) (0·59 g.) was obtained after chromatography; its properties including infrared absorption were identical with those of previous samples.

Formation of Aldehydes from Tertiary Amines.—A solution of the amine (0·002 mole) in the desired solvent (5 c.c.) was added to benzoyl peroxide (0·001 mole) in the same solvent (5 c.c.) at 20°. The reaction was taken as complete when the bulk of the peroxide had been consumed, as indicated by the greatly diminished intensity of the blue colour produced by a sample on mixing with triethylamine and 2 : 5-dichloro-3 : 6-dimethoxy-*p*-benzoquinone (test reaction as above). The yields of aldehydes were estimated as 2 : 4-dinitrophenylhydrazones after addition of an excess of the reagent sulphate in methanol (see Table).

Amine	Solvent	Reaction time (hr.)	2 : 4-Dinitrophenylhydrazone (%)
$Ph\cdot CH_2\cdot NMe_2$	Benzene	9	56, 53
$Ph\cdot CH_2\cdot NMe_2$	Dioxan	8	47
p-$MeO\cdot C_6H_4\cdot CH_2\cdot NMe_2$	Benzene	1·5	56, 60
p-$NO_2\cdot C_6H_4\cdot CH_2\cdot NMe_2$	Benzene	5	47
NPr^n_3	Dioxan–H_2O (9 : 1)	1·5	39 *

* Unused peroxide (60%) was recovered from this experiment.

Dinitrophenylhydrazines of the following were obtained (each gave a satisfactory analysis): benzaldehyde, m. p. 242—244·5° (from dioxan–ethyl acetate), *p*-anisaldehyde, m. p. 254—255° (from dioxan), *p*-nitrobenzaldehyde, m. p. 334° (from pyridine–methanol), and propionaldehyde, m. p. 153—157° (from ethanol).

Comparative Reaction Rates.—Equal volumes of solutions of the amine (0·4M) and benzoyl peroxide (0·2M) in benzene were mixed, introduced immediately into a 1 mm. cell, and the infra-red absorption in the 1900—1600 cm.$^{-1}$ range repeatedly determined. As the peaks at 1785 and 1762 cm.$^{-1}$ due to benzoyl peroxide diminished, a new maximum at 1705 cm.$^{-1}$ developed: the times at which the heights of the 1762 and 1705 cm.$^{-1}$ peaks became equal are as annexed, the temperature of the mixture being in each case 20°.

Amine	Time (min.)	Amine	Time (min.)
Triethylenediamine	<1	NPr^n_3	9·25
NMe_3	1·5	$Ph\cdot CH_2\cdot NMe_2$	9·75
NEt_3	8·0	$N(CH_2Ph)_3$	>19 days

Within 1 hr., the solutions from those amines (triethylamine, tripropylamine) which can give enamines became yellow, then orange, then brown. The other reaction solutions remained colourless.

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