591. *Amine Oxidation. Part I. The Side-chain Oxidation of* N-*Alkyl- and* NN-*Dialkyl-anilines by Manganese Dioxide.*

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Alkyl- and dialkyl-anilines are oxidised by manganese dioxide at room temperature, the three reactions discerned being (*a*) amide formation, (*b*) dealkylation with formation of an aliphatic aldehyde, and (*c*) dehydrogenation followed by oxidative cleavage of the resultant enamine. With many amines the reaction takes essentially a single course and good yields of oxidation products can be isolated.[1]

The oxidising power of solid manganese dioxide is shown to vary with the reaction under examination.

APART from the report [2] that hydrohydrastinine is not oxidised by manganese dioxide and a preliminary account [3] of the oxidation of the alkaloid, tazettine, the possibilities of oxidising *tert.*-amines with this reagent do not seem to have been investigated. The present study developed from the observation that an exothermic reaction took place on addition of manganese dioxide to dimethylaniline * at 20°. The crude product exhibited

$$Ph \cdot NMe_2 \longrightarrow Ph \cdot NMe \cdot CHO \quad (I)$$

carbonyl absorption near 1680 cm.$^{-1}$, and subsequent isolation of *N*-methylformanilide (I) confirmed the oxidation of a side-chain methyl group. After a suitable general procedure
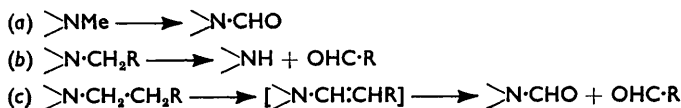
* In this paper, all mono- and di-alkylanilines are the *N*-alkylated compounds.

[1] Cf. *Chem. and Ind.*, 1956, 1097.
[2] Highet and Wildman, *J. Amer. Chem. Soc.*, 1955, **77**, 4399.
[3] *Idem, Chem. and Ind.*, 1955, 1159.

had been developed, various alkylated anilines were submitted to oxidation, and from these experiments three main types of conversion have been discovered :
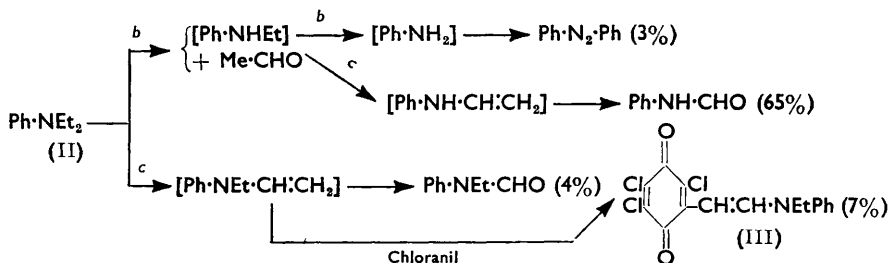
(a) $>$NMe $\longrightarrow$ $>$N·CHO

(b) $>$N·CH$_2$R $\longrightarrow$ $>$NH + OHC·R

(c) $>$N·CH$_2$·CH$_2$R $\longrightarrow$ [$>$N·CH:CHR] $\longrightarrow$ $>$N·CHO + OHC·R

Conversion (a) is well exemplified by the oxidation of dimethylaniline to N-methyl-formanilide in nearly 80% yield. Monomethylaniline was oxidised analogously, giving formanilide in over 80% yield. Azobenzene (2·5%) was also isolated from this last reaction : its formation is thought to be due to dealkylation (conversion b) to aniline, which is then oxidised to the azo-compound; this type of oxidation has been effected with several aromatic primary amines, including aniline.[4]

Introduction of the *p*-methyl group into dimethylaniline somewhat facilitated (see below) the oxidation to the N-formyl compound, but a *p*-nitro-substituent completely inhibited the reaction at room temperature. Thus it appears that the " availability " of electrons on nitrogen is of importance in promoting the reaction, and is analogous to the relative stability of N-acyl anilines, the end-products of most of the present oxidations. In the case of *p*-nitrodimethylaniline, preferential adsorption of the nitro-group on to the oxide surface might also be inhibiting the reaction.

In the oxidation of diethylaniline (II), conversion (b) became the predominant initial reaction, acetaldehyde (54%) being isolated by passing nitrogen through the reaction mixture. Stages in the formation of oxidation products from this amine may be represented at present as annexed.

Oxidation of the more highly branched *iso*propyl- and *tert.*-butyl-anilines (kindly supplied by Dr. T. H. H. Quibell) gave highly coloured polymeric materials.

Among the reagents previously shown to dehydrogenate tertiary amines may be mentioned chromic acid,[5] mercuric acetate,[6] and halogenated *p*-benzoquinones.[7] Dehydrogenation of ethylaniline to the vinylaniline is at present postulated to explain the

Ph·NEt$_2$ —
(II)

b $\begin{cases}$[Ph·NHEt] $\longrightarrow$ [Ph·NH$_2$] $\longrightarrow$ Ph·N$_2$·Ph (3%)$\\$+ Me·CHO$\end{cases}$ c

[Ph·NH·CH:CH$_2$] $\longrightarrow$ Ph·NH·CHO (65%)

c [Ph·NEt·CH:CH$_2$] $\longrightarrow$ Ph·NEt·CHO (4%)

Chloranil

Cl—CH:CH·NEtPh (7%)
(III)

formation of formanilide : the possible involvement of other intermediates such as N-ethylideneaniline cannot be discussed on the evidence so far available.

In agreement with the main route postulated by us, separate oxidation of mono-ethylaniline afforded formanilide (70%), with smaller quantities of acetaldehyde and azobenzene. The minor amide product from diethylaniline was N-ethylformanilide formed by conversion (c). Evidence for an enamine intermediate in this oxidation was obtained by a reaction in the presence of chloranil with which the enamine afforded the blue quinone [7] (III). (The oxidation of another enamine is described below.)

Conversions (a) and (b) being the major routes for the oxidation of dimethyl- and diethyl-aniline respectively, it was not surprising to find that ethylmethylaniline (IV)

[4] Haslam and Quibell, unpublished work; Haslam, Ph.D. Thesis, Manchester, 1953.
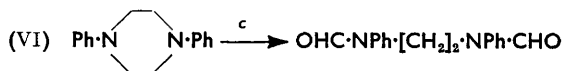[5] Willstätter and Marx, *Ber.*, 1905, **38**, 1772.
[6] Leonard, Millar, and Thomas, *J. Amer. Chem. Soc.*, 1956, **78**, 3463, and earlier papers.
[7] Buckley and Henbest, *Chem. and Ind.*, 1956, 1096.

underwent both types of reaction. 1-Phenylpyrrolidine, structurally related to diethyl-aniline, also gave formanilide on oxidation, but the yield was lower (48%).

$$Ph \cdot NEt \cdot CHO \xleftarrow{a} Ph \cdot NMeEt \text{ (IV)} \xrightarrow{b} [Ph \cdot NHMe] \longrightarrow Ph \cdot NH \cdot CHO$$
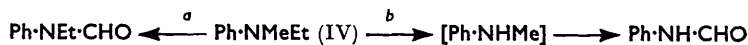
The presence of the nitrogen atom is obviously essential for the occurrence of dehydrogenation (conversion c) under these mild conditions, and in the expectation that a

$$\text{(V)} \quad Ph \cdot NMe \cdot [CH_2]_2 \cdot NPhMe \xrightarrow{c} 2Ph \cdot NMe \cdot CHO$$

$$\text{(VI)} \quad Ph \cdot N\underset{}{\overset{\frown}{}}N \cdot Ph \xrightarrow{c} OHC \cdot NPh \cdot [CH_2]_2 \cdot NPh \cdot CHO$$

second amino-grouping in a β-position should promote this type of reaction, the diamines (V) and (VI) were prepared. Both gave high yields of N-formyl compounds.

$$\text{(VII)} \quad Ph \cdot CH\text{:}CH \cdot N(CH_2Ph)_2 \longrightarrow Ph \cdot CHO + OHC \cdot N(CH_2Ph)_2$$
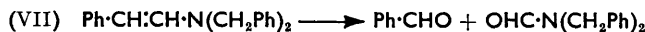
Further evidence for the enamine fission postulated as the second stage of conversion (c) was obtained by oxidation of NN-dibenzylstyrylamine (VII) which very readily gave the expected products. Hydroxylation is an obvious initial stage in the enamine fission and
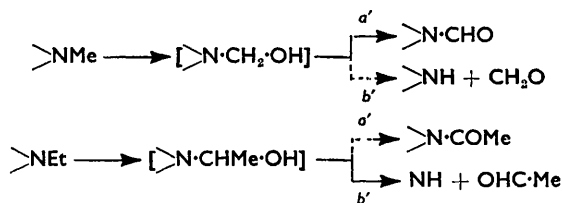
$$\text{(VIII)} \quad Bu^nO \cdot CH\text{:}CH_2 \longrightarrow [Bu^nOH] \longrightarrow Me \cdot CH(OBu^n)_2 \quad \text{(IX)}$$

vic.-glycols are known [8] to be cleaved by manganese dioxide. The rapid cleavage of the enamine (VII) suggested that a compound containing a similar ether system should also be oxidised. *n*-Butyl vinyl ether (VIII) on treatment with manganese dioxide yielded

$$\text{(X)} \quad Ph \cdot N\underset{}{\overset{\frown}{}}O \xrightarrow{c} OHC \cdot NPh \cdot CH_2 \cdot CH_2 \cdot OH \quad \text{(XI)}$$
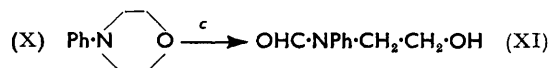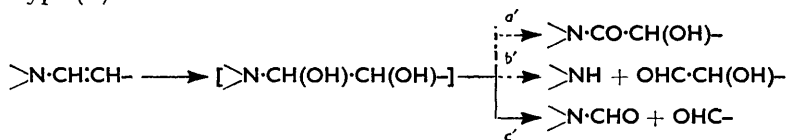
acetaldehyde di-*n*-butyl acetal (IX), clearly formed by addition of the intermediate butanol to unchanged vinyl ether. 4-Phenylmorpholine (X) containing amine and ether functions, afforded the N-formyl-alcohol (XI) in high yield.

A somewhat more detailed discussion of some of these reactions may be made in terms of hydroxylated intermediates. It seems not unlikely that carbinolamines can be formed as intermediates, the ensuing fate of each carbinolamine depending on its structure; for the carbinolamines from N-methyl and N-ethyl compounds, a choice between reaction paths (a') and (b') is available :

$$\text{>NMe} \longrightarrow [\text{>N} \cdot CH_2 \cdot OH] \xrightarrow[b']{a'} \begin{array}{l} \text{>N} \cdot CHO \\ \text{>NH} + CH_2O \end{array}$$

$$\text{>NEt} \longrightarrow [\text{>N} \cdot CHMe \cdot OH] \xrightarrow[b']{a'} \begin{array}{l} \text{>N} \cdot COMe \\ \text{NH} + OHC \cdot Me \end{array}$$
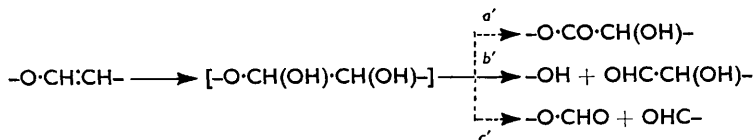
The relative rates of these two reactions will depend on steric and other factors which need not be discussed at present.

In the second stage of conversion (c), cleavage (c') of the intermediate glycol structure is evidently more rapid than its oxidation by a reaction of type (a') or isomerisation by a reaction of type (b') :

$$\text{>N} \cdot CH\text{:}CH- \longrightarrow [\text{>N} \cdot CH(OH) \cdot CH(OH)-] \begin{array}{l} \xrightarrow{a'} \text{>N} \cdot CO \cdot CH(OH)- \\ \xrightarrow{b'} \text{>NH} + OHC \cdot CH(OH)- \\ \xrightarrow{c'} \text{>N} \cdot CHO + OHC- \end{array}$$
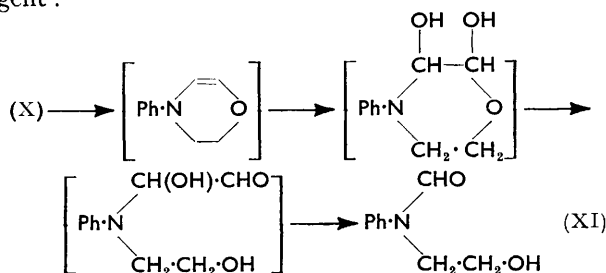
[8] Padilla and Herràn, *Bol. Inst. Quím. Univ. nac. auton. México*, 1956, **8**, 3.

On the other hand, in the second stage of the oxidation of unsaturated ethers (*e.g.*, VIII), formation of an alcohol from the glycol (*b'* reaction) can be assisted by the greater ease of separation of the oxy-anion (−OH more acidic than >NH) :

$$-O \cdot CH:CH- \longrightarrow [-O \cdot CH(OH) \cdot CH(OH)-] \begin{cases} \xrightarrow{a'} -O \cdot CO \cdot CH(OH)- \\ \xrightarrow{b'} -OH + OHC \cdot CH(OH)- \\ \xrightarrow{c'} -O \cdot CHO + OHC- \end{cases}$$

This scheme appears to provide the best explanation for the intermediate formation of butan-1-ol from *n*-butyl vinyl ether (VIII); the possibility that the alcohol arises by further oxidation of *n*-butyl formate (formed by a *c'*-type reaction from the initial glycol derivative) can be ruled out by the comparative stability of this ester to the oxidising agent.   The oxidation of 4-phenylmorpholine (X) may now be envisaged as follows, previous work [8] having shown that compounds containing a −CH(OH)·CO− grouping are cleaved by the reagent :

$$(X) \longrightarrow \left[Ph \cdot N \underset{}{\overset{}{\bigcirc}} O \right] \longrightarrow \left[\begin{array}{c} \overset{OH \ \ OH}{\underset{}{CH-CH}} \\ Ph \cdot N \qquad O \\ CH_2 \cdot CH_2 \end{array} \right] \longrightarrow$$

$$\left[\begin{array}{c} CH(OH) \cdot CHO \\ Ph \cdot N \\ CH_2 \cdot CH_2 \cdot OH \end{array} \right] \longrightarrow \begin{array}{c} CHO \\ Ph \cdot N \\ CH_2 \cdot CH_2 \cdot OH \end{array} \qquad (XI)$$

The essential features of the oxidation of tazettine [3] may be represented as :

$$>C(OH) \cdot CH_2 \cdot NMeR \longrightarrow [>C(OH) \cdot CH(OH) \cdot NMeR] \longrightarrow >CO + OHC \cdot NMeR$$
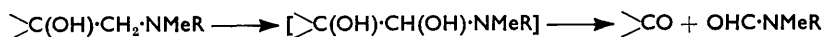
As amine oxides can be isomerised to secondary amines and carbonyl compounds (probably *via* carbinolamines) in the presence of some metallic salts,[9] the *N*-oxides of dimethyl- and diethyl-aniline were treated with manganese dioxide in order to test the possibility that conversions (*a*) and/or (*b*) proceeded *via* such intermediates.   Dimethylaniline *N*-oxide was recovered unchanged, showing that it was not involved as an intermediate in the formation of *N*-methylformanilide.   Diethylaniline *N*-oxide gave formanilide in lower yield (25%) than the parent amine and it seems, therefore, that there must be another route available for the production of formanilide from the tertiary amine.

The general procedure for the oxidation of the alkylanilines was to stir a chloroform solution of the amine with the dioxide, an amine : dioxide ratio of 1 : 50 being used; this large ratio had been found to be necessary to give complete oxidation of dimethylaniline. However, for dimethyl-*p*-toluidine less oxide was necessary.   In this way a comparison of various reactions has shown that the amount of oxygen available from a given weight of manganese dioxide varies with the nature of the organic substrate.

The following approximate amounts of manganese dioxide afford 16 g. of available oxygen for oxidation of the given organic compounds :

Dioxide (g.)	Substance	Dioxide (g.)	Substance	Dioxide (g.)	Substance
600 [a]	Tetrachloroquinol	950	NH_2Ph [4]	3000	$NPhMe_2$
800 [b]	Allylic alcohols	1500	(VII)	23,000 [a]	$CH_2Ph \cdot NMe_2$
		2700	p-$C_6H_4Me \cdot NMe_2$		

[a] Unpublished work.   [b] Average value computed from the literature, including ref. 4.

Thus only a small fraction of the oxygen in manganese dioxide is available for the oxidation of organic compounds at room temperature.   Various other metal oxides (see p. 3038)

[9] Diels and Fischer, *Ber.*, 1916, **49**, 1721; Fish, Johnson, and Horning, *J. Amer. Chem. Soc.*, 1956, **78**, 3668.

have been shown not to oxidise dimethylaniline. The peculiar effectiveness of manganese dioxide may in part be related to the fact that as ordinarily prepared by precipitation it is a " non-stoicheiometric compound." [10] Products prepared by reduction of permanganates in aqueous solution, followed by drying at moderate temperatures (*e.g.*, 100°), have oxygen contents slightly less than that corresponding to the dioxide, and also contain water (3—4%) which cannot be removed thermally without some further loss of oxygen. This " water " is probably present as hydroxyl groups linked to manganese. The formation of hydroxylated amine intermediates (suggested above) may be assisted, if not caused, by these hydroxyl groups in the dioxide.

Some preliminary observations have also been made which indicate that the amount of available oxygen in the dioxide may depend on its method of preparation (for similar observations with allylic alcohols, see ref. 11). In particular, the oxidising power of the reagent diminished after it had been washed with sulphurous acid. Washing the dioxide with permanganate solution had no appreciable effect.

The possibility that the oxidising properties result from contribution of a small " proportion " of manganese in a higher valency state led to some experiments on the oxidation of dimethylaniline with potassium permanganate under various conditions. *N*-Methylformanilide was also obtained with this oxidising agent * but the yields were low. The best procedure evolved was to shake the amine in benzene with an aqueous solution of the oxidising agent. After 20 hr. the amide was obtained in 24% yield together with unchanged amine (54%). For this oxidation permanganate offers no advantage over the more efficient manganese dioxide.

EXPERIMENTAL

The infrared absorption spectra of the products were consistent with the structures assigned.

Manganese dioxide used was a commercial sample, from Messrs. J. Woolley, Sons and Co. Ltd. who state that it was prepared by mixing solutions of a bivalent manganese salt and a permanganate, *i.e.*, under acidic conditions.

Manganese Dioxide Oxidation of Tertiary Amines.—The amine (3 g.) in chloroform (300 c.c.) was stirred with manganese dioxide (150 g.) for 18 hr. at 20°. The oxide was removed and washed with chloroform. The organic extract was washed with dilute hydrochloric acid and evaporated. The residue was usually distilled in order to remove small quantities of coloured, less volatile material.

(*a*) In this way, dimethylaniline gave *N*-methylformanilide (2·58 g., 78%), b. p. 121°/15 mm., m. p. and mixed m. p. 13°, n_D^{19} 1·5598.

(*b*) Methylaniline afforded a product (3·08 g.), part of which (1·45 g.) was distilled under reduced pressure. The distillate crystallised from benzene–light petroleum at −20°, to give formanilide (1·33 g., 83%), m. p. and mixed m. p. 49°. The remainder of the crude product was chromatographed on alumina (80 g.), elution with benzene affording azobenzene (30 mg.), m. p. and mixed m. p. 67—68°.

(*c*) Distillation of the product from oxidation of diethylaniline afforded material which on crystallisation from toluene–light petroleum at −20° gave formanilide (1·58 g., 65%), b. p. 90°/13 mm., m. p. and mixed m. p. 49° (Found : C, 69·5; H, 5·9. Calc. for C_7H_7ON : C, 69·5; H, 5·8%). In another experiment, diethylaniline (2 g.) afforded crude material (1·7 g.), part (0·9 g.) of which was distilled. The solid distillate was extracted with light petroleum at 20°, to give (after removal of the solvent) crude *N*-ethylformanilide (50 mg.) as a yellow oil. This was reduced in ether (20 c.c.) with lithium aluminium hydride (50 mg.), being stirred overnight at 20°. The basic product was isolated in the usual way and treated with picric acid (80 mg.) in benzene (30 c.c.). Crystallisation from benzene yielded ethylmethylaniline picrate (103 mg.),

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* Amides are among the products obtained by permanganate oxidation of many alkaloids containing tertiary aliphatic amine groupings. For two recent examples see ref. 12.

[10] Sidgwick, " Chemical Elements and their Compounds," Clarendon Press, Oxford, 1950, p. 1272; Wells, " Structural Inorganic Chemistry," Clarendon Press, Oxford, 1950, p. 371.

[11] Attenburrow, Cameron, Chapman, Evans, Hems, Jansen, and Walker, *J.*, 1952, 1094; Harfenist, Bavley, and Lazier, *J. Org. Chem.*, 1954, **19**, 1608.

[12] Pelletier and Jacobs, *J. Amer. Chem. Soc.*, 1954, **76**, 4496; Cookson and Trevett, *J.*, 1956, 2689.

m. p. and mixed m. p. 127—128°. The remainder (0·8 g.) of the crude oxidation product was chromatographed on alumina as before, to give azobenzene (16 mg.), m. p. and mixed m. p. 66—68°.

(*d*) The crude product from ethylaniline was treated as described above for methylaniline, one part (1·27 g.) affording formanilide (1·04 g., 70%), m. p. and mixed m. p. 48—49°, and the remainder (1·28 g.) azobenzene (50 mg.), m. p. and mixed m. p. 68°.

(*e*) Oxidation of ethylmethylaniline gave a product (2·4 g.) which was separated into fractions by distillation under reduced pressure. The first, liquid fractions (0·50 g., 16%) consisted of *N*-ethylformanilide as shown by infrared absorption spectra. Later fractions solidified, and formanilide (1·68 g., 63%), m. p. and mixed m. p. 49°, was obtained by crystallisation.

(*f*) Oxidation of 1-phenylpyrrolidine afforded formanilide (1·2 g.), m. p. and mixed m. p. 49°.

(*g*) The crude material (1 g.) from oxidation of 1 : 4-diphenylpiperazine (1 g.) was filtered in chloroform through deactivated alumina (10 g.), and then crystallised from benzene–light petroleum, to give *NN'*-diformyl-*NN'*-diphenylethylenediamine (0·9 g., 80%), m. p. 121—122° (Found : C, 72·2; H, 6·1. Calc. for $C_{16}H_{16}N_2O_2$: C, 71·65; H, 6·0%) (lit.,[13] m. p. 121—122°).

(*h*) Oxidation of 1 : 2-dimethyl-1 : 2-diphenylethylenediamine yielded *N*-methylformanilide (2·47 g., 75%), b. p. 120°/15 mm., m. p. and mixed m. p. 12°.

(*i*) Preliminary experiments showed that the oxidation of *NN*-dibenzylstyrylamine required less manganese dioxide; the enamine (1 g.) was stirred in chloroform (200 c.c.) with manganese dioxide (10 g.) for 30 min. The infrared spectrum of the crude product (0·94 g.) showed that starting material was absent. Part (200 mg.) of this product gave benzaldehyde 2 : 4-dinitrophenylhydrazone (166 mg., 77%), m. p. and mixed m. p. 237°. Another part (500 mg.) was shaken with aqueous sodium hydrogen sulphite (30 c.c.) and ether. Evaporation of the ether gave material (350 mg.) which on crystallisation from benzene–light petroleum afforded *NN*-dibenzylformamide (300 mg., 75%), m. p. and mixed m. p. 52°.

(*j*) The solid product from the oxidation of 4-phenylmorpholine (5 g.) by the general method was crystallised from benzene to give N-*formyl*-N-2-*hydroxyethylaniline* (4 g., 80%), m. p. 58·5° (Found : C, 65·45; H, 6·6; N, 8·5. $C_9H_{11}O_2N$ requires C, 65·45; H, 6·7; N, 8·5%). A solution of potassium hydroxide (4 g.) in water (10 c.c.) containing the formyl compound (0·2 g.) was heated under reflux for 3 hr. Isolation with ether afforded *N*-2-hydroxyethylaniline (0·15 g.), identified by comparison of its infrared spectrum with that of an authentic sample prepared from aniline and ethylene oxide.

By the general procedure, dimethylaniline was not oxidised significantly by ceric oxide, lead dioxide, cuprous oxide, or titanium dioxide.

Acetaldehyde from the Oxidation of Diethylaniline.—The amine (1 g.) in benzene (300 c.c.) was stirred with manganese dioxide (50 g.) for 15 hr. At the same time nitrogen was passed through the mixture and thence into a solution of dimedone in 1 : 4 ethanol–water (250 c.c.). The yields of acetaldehyde derivative (m. p. and mixed m. p. 138—139°) were 1·08 g. and 1·2 g. in two experiments (average 54%).

Detection of the Enamine Intermediate in the Oxidation of Diethylaniline.—A solution of the amine (2 g.) and chloranil (3·3 g.) in benzene (270 c.c.) was stirred with manganese dioxide : in four experiments the amounts of dioxide used were 10, 20, 40, and 100 g. Samples of the blue solution were withdrawn from time to time and washed with dilute sulphuric acid and the absorption measured at 6400 Å. In this way the dependence of the yield of blue quinone (III) with time and dioxide : amine ratio was determined :

Oxide : amine ratio	Time (hr.) for complete formation of quinone	Yield (%) of blue quinone at this time
5	4	6·3
10	2	7
20	0·5	4·5
50	—	—

The optimum amount of blue quinone (based on starting amine) was formed with an oxide : amine ratio of 10, larger quantities of dioxide oxidising some or all of the quinone. In the absence of manganese dioxide the yield of blue quinone was less than 0·1%.

The final solution from the second experiment was filtered and washed with dilute sulphuric

[13] Zienty, *J. Amer. Chem. Soc.*, 1946, **68**, 1388.

acid, and the product chromatographed on deactivated alumina. Benzene first eluted unchanged chloranil and then 2-2′-N-*ethylanilinovinyl*-3 : 5 : 6-*trichlorobenzoquinone* (III), m. p. 127—129° (from benzene) (Found : C, 54·0; H, 3·25. $C_{16}H_{12}O_2NCl_3$ requires C, 53·85; H, 3·35%), $\lambda_{max.}$ (in EtOH) 6400 Å (ε 10,100).

Other Oxidation Experiments with Dimethylaniline.—Variation of the oxide : amine weight ratio gave the following results :

Oxide : amine ratio	10	20	40	50	60
Amine recovered (%)	77	40	12	0	0
Ph·NMe·CHO (%)	6·5	25	58	77	78

Very similar yields of N-methylformanilide were obtained by using the oxide recovered from treatment with saturated aqueous potassium permanganate solution at 20° for 6 hr., followed by washing with water until the filtrate was colourless and drying *in vacuo* at 20°. With an oxide : amine ratio of 10, the yield was decreased to 2% by using the oxide after it had been stirred with an aqueous solution of sulphur dioxide for 1 hr. and then dried as before.

Permanganate Oxidations.—(*a*) A slightly exothermic reaction took place on addition of potassium permanganate (4 g.) in acetic acid (250 c.c.) to a stirred solution of dimethylaniline (5 g., *i.e.* excess) in acetic acid (30 c.c.), and a brown solution was obtained. After most of the acetic acid had been removed under reduced pressure, the residue was made alkaline (manganese dioxide precipitated) and extracted with chloroform. Isolation in the standard way gave N-methylformanilide (0·3 g., 12% based on permanganate), m. p. and mixed m. p. 13°, n_D^{19} 1·6000.

(*b*) Silica gel (200 g.) was immersed in a saturated aqueous solution of potassium permanganate, allowed to drain, and dried *in vacuo* at 20°. Titration showed that the gel contained 2·5 g. of permanganate. This impregnated material was stirred with a solution of the amine (5 g., excess) in benzene (300 c.c.) for 20 hr., whereafter no permanganate remained. Isolation as before afforded N-methylformanilide (0·1 g., 6% based on permanganate), m. p. and mixed m. p. 13°, and unchanged amine (4·6 g.).

(*c*) A solution of the amine (5 g.) in benzene (250 c.c.) was rolled with finely powdered permanganate (20 g.) and steel balls for 3 days. Working up as before gave N-methylformanilide (0·33 g., 6% based on amine), m. p. and mixed m. p. 12·8°, and unchanged amine (3·2 g.). Repetition of the experiment with twice as much permanganate afforded amide (0·4 g., 7%) and amine (3·96 g.).

(*d*) A solution of the amine (5 g.) in benzene (120 c.c.) was shaken vigorously with a solution of potassium permanganate (30 g.) in water (300 c.c.) for 20 hr. The manganese dioxide formed was removed (unchanged permanganate was present in the aqueous layer). N-Methylformanilide (1·3 g., 24% conversion), m. p. and mixed m. p. 13°, and unchanged amine (2·7 g., 54%) were isolated.

Dimethyl-p-toluidine. Variation of Oxide : Amine Ratio.—The following results were obtained :

Oxide : amine ratio	10	18	23	40
Amine recovered (%)	63	22	13	0
N-Formyl compound (%)	21	54	66	84

Experiments with N-Oxides.—Dimethylaniline N-oxide (1 g.) was treated with manganese dioxide by the above general procedure. Removal of the solvent under reduced pressure gave a brown gum which was dissolved in water (50 c.c.) and extracted with ether. The ether layer was washed with dilute hydrochloric acid, dried, and evaporated to afford a residue (30 mg., 3%) which appeared from its infrared spectrum to be essentially N-methylformanilide. The aqueous layer was treated with picric acid (2 g.) in hot water (50 c.c.), to give dimethylaniline N-oxide picrate (2 g., 90%), m. p. and mixed m. p. 135—137°.

Diethylaniline N-oxide (0·33 g.) was treated with manganese dioxide by the above general method. The non-basic product was obtained as dark viscous gum (120 mg.) which was filtered in chloroform through alumina (8 g.) to give material (100 mg.) which left an amorphous, probably polymeric material (15 mg., m. p. 65—120°) on trituration with toluene–light petroleum (1 : 1) at 20°. The mother-liquor was cooled to −70°, to give formanilide (60 mg., 25%), m. p. and mixed m. p. 47—49°.

Oxidation of n-*Butyl Vinyl Ether.*—Oxidation of the ether (3 g.) by the general method gave acetaldehyde di-*n*-butyl acetal (2·1 g., 80%), b. p. 190°/760 mm., n_D^{19} 1·4121 (Found : C, 68·8; H, 12·3. Calc. for $C_{10}H_{22}O_2$: C, 69·0; H, 12·65%) [lit.,[14] b. p. 197—198°/760 mm., n_D^{26} 1·4090]. The infrared spectrum exhibited a strong doublet at 1100 and 1140 cm.$^{-1}$. On treatment with 2 : 4-dinitrophenylhydrazine the derivative of acetaldehyde was formed (m. p. and mixed m. p. 165—166°).

Attempted oxidation of *n*-butyl formate by the general method gave unchanged ester (94%).

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[14] Hinton and Nieuwland, *J. Amer. Chem. Soc.*, 1930, **52**, 2892.