Amine Oxidation and the Chemistry of Quinone Imines. Part II.[1] 2,5-Dimethoxy-4-t-butylaniline

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The oxidation of 2,5-dimethoxy-4-t-butylaniline (1) by alkaline ferricyanide or silver oxide gives 2,2',5,5'-tetramethoxy-4,4'-di-t-butylazobenzene (2) and 3,8-dimethoxy-2,7-di-t-butylphenazine (3). Chromatographic separation of the oxidation products on neutral alumina gives rise to six other products, including three *N*-aryl-*p*-quinone imines (4), (6), and (7), a tetrameric product (5), and a phenoxazone (8). Evidence is presented for the structures of these compounds, and their origin is discussed.

The formation of the phenazine (3) provides clear evidence for the cyclisation of an intermediate *N*-aryl-*o*-quinone di-imine (11) under these conditions. Isolation of the debutylated quinone imine (7) substantiates assumptions made in the previous paper.

THE oxidation of 2-anilinoanilines bearing a replaceable substituent, such as halogen or an alkoxy-group, in the 2'-position invariably results in the formation of a phenazine, with the elimination of this substituent.[2] It has also been reported recently that oxidation of 5-t-butyl-*o*-anisidine [3,4] and 5-t-butyl-*o*-phenetidine [4] with lead dioxide in refluxing benzene gives 2,7-di-t-butylphenazine. This result is of interest as the presence of the *o*-alkoxy-group would prevent the formation of an intermediate 2-anilinoaniline, and it seems likely that under these conditions the expected *N*-phenyl-*o*-quinone di-imine intermediate would have undergone thermally induced cyclisation. To establish unequivocally whether such di-imines can cyclise to phenazines under the conditions of ferricyanide or silver oxide oxidation—a reaction that appeared not to take place during oxidation of 3-methoxy-4-t-butylaniline [1]—we have examined the oxidation of 2,5-dimethoxy-4-t-butylaniline (1), in which formation of a 2-anilinoaniline is similarly prevented. This amine was chosen because the expected phenazine (3) was available [1] and other oxidation products could readily be related to those of the monomethoxy-analogue.[1]

Oxidation of the aniline (1) with alkaline ferricyanide

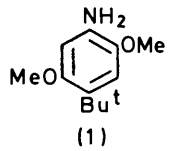
[1] Part I, R. K. Haynes and F. R. Hewgill, preceding paper.

[2] G. A. Swan and D. G. I. Felton, ' The Chemistry of Heterocyclic Compounds, Phenazines,' Interscience, New York, 1957, p. 6.

[3] F. N. Mazitova and R. R. Shagidullin, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1966, 1851 (*Chem. Abs.*, 1957, **66**, 75,774b).

[4] F. N. Mazitova, R. R. Shagidullin, and V. V. Abushaeva, *Zhur. org. Khim.*, 1967, **3**, 878 (*Chem. Abs.*, 1967, **67**, 43,137a).

and with silver oxide gave the products (2)—(8) in the yields shown. As in the previous oxidation,[1] unchanged aniline was always present at the end of the reaction time when ferricyanide was used as oxidant, and none of the quinonoid materials (4)—(8) were detected before chromatographic fractionation of either oxidation mixture. Yields of the tetrameric compound (5) and of the phenoxazone (8) were not reproducible.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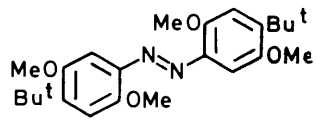
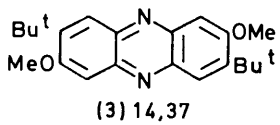
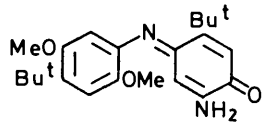
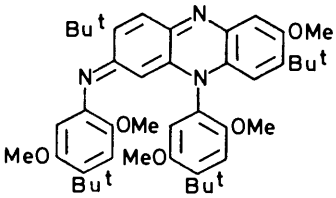
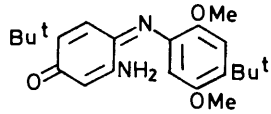
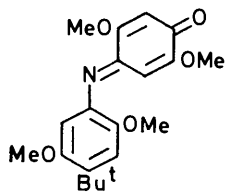

(2) 15,14

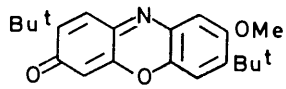

(3) 14,37


(4) 0·8,0


(5) *ca.* 3,0


(6) 0,0·1

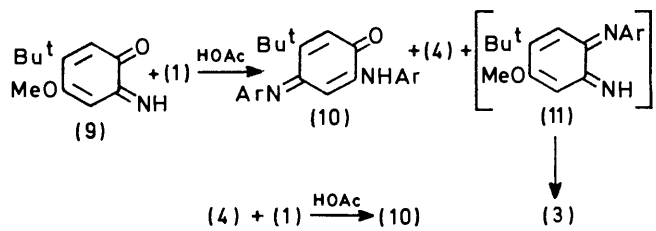

(7) 0·3,0·5


(8) *ca.* 3,0·4

Figures represent yields (%) [$K_3Fe(CN)_6$, Ag_2O]

Product Identification.—The azobenzene (2) was identified spectrally, and synthesised by coupling diazotised 2,5-dimethoxy-4-t-butylaniline with 4-methoxy-3-t-butylphenol and methylating the product. The phenazine (3) produced was identical with the previously obtained product.[1]

Like the corresponding product from 3-methoxy-4-t-butylaniline, the amino-quinone imine (4) could not be crystallised, but was similarly synthesised. Condensation of the aniline (1) with 6-imino-4-methoxy-3-t-butylcyclohexa-2,4-dien-1-one (9) gave the quinone imine (4) in 4% yield. The major product of this condensation was compound (10), which was identified by its n.m.r. and i.r. spectra, and was also formed by acid-catalysed condensation of the amino-quinone imine (4) with (1). A small amount (1%) of the phenazine (3) was also isolated from the condensation of (9) with (1), indicating that some addition of the aniline (1) had taken place at the carbonyl group of (9) to produce the di-imine (11), which had subsequently cyclised (Scheme 1).



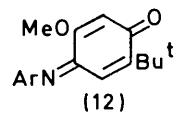
Ar = 2,5-$(OMe)_2$-4-$Bu^tC_6H_2$

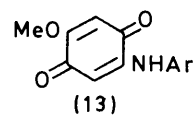
SCHEME 1

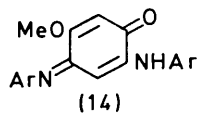
The assignment of structure (5) to the deep, indigo-blue product obtained from the ferricyanide oxidation is based on the n.m.r. spectrum, which contained signals from eight uncoupled ring protons, five methoxy-groups, and four t-butyl groups. Amine and quinone-carbonyl absorptions were absent from the i.r. spectrum. This material was formed when compound (10) was condensed with the aniline (1).

Compound (6) is the dimethoxy-analogue of the amino-quinone imine described in Part I,[1] which showed similar spectral characteristics. It was obtained in 16% yield by condensation of 2-amino-5-t-butyl-1,4-benzoquinone with (1).

The structure of compound (7) appears to be unambiguously suggested by its n.m.r. spectrum, which displayed signals attributable to two aromatic and two vinylic protons, separate signals for four methoxy-groups, and only one t-butyl resonance. The i.r. spectrum showed a single carbonyl absorption at 1652 cm^{-1}, and the u.v. spectrum [$\lambda_{max.}$ (log ε) 213 (4·29), 298 (4·36), and 487 (3·43) nm] was similar to that of the synthetic quinone imine (12) [$\lambda_{max.}$ (log ε) 218 (4·04), 294 (4·22), and 510 (3·43) nm].


(12)


(13)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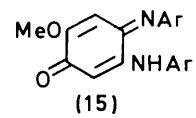
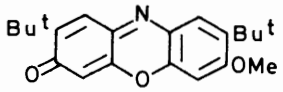

(15)

Ar = 2,5-$(OMe)_2$-4-$Bu^tC_6H_2$

It was hoped that acid-catalysed condensation of the aniline (1) with 2,5-dimethoxy-*p*-benzoquinone would give (7), but in hot acetic acid two different products were obtained. The first was identified as the anilino-quinone (13) by the presence of secondary amine (3320 cm^{-1}) and quinonoid (1662 and 1647 cm^{-1}) bands in its i.r. spectrum, and by the n.m.r. spectrum, which contained one t-butyl and three methoxy-signals. Spectroscopic evidence indicated that the second compound possessed structure (14) or (15), but a distinction could not be made on this ground alone. However, when the

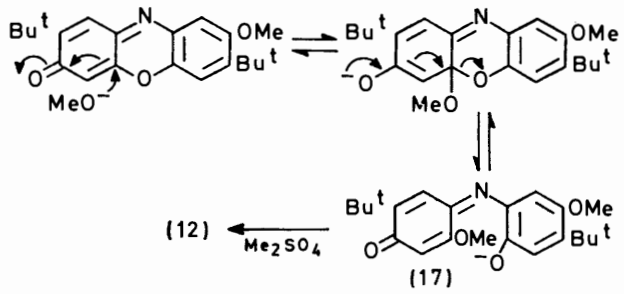
quinone imine (7) was condensed with (1) in cold acetic acid, this material [(14) or (15)] was the sole product. This result is consistent with the proposed structure (7).

The n.m.r. spectrum of the last quinonoid oxidation product (8) indicated the presence of two-t-butyl groups, one methoxy-group, and two vinylic and two aromatic protons. The i.r. spectrum, with absorptions at 1641 and 1613 cm^{-1}, indicated the presence of a quinonoid carbonyl group.[5] As empirical analysis showed that three oxygen atoms were present, one of these must be ring-bridging, and this was confirmed by reductive acetylation. The resultant diacetate had i.r. absorptions attributable to *O*-acetyl (1766 cm^{-1}) and tertiary amide (1611 cm^{-1}) groups, and hence the only structures that fit the evidence are those of the two phenoxazones (8) and (16). The u.v. spectrum [$\lambda_{max.}$ 223, 263, 359, and 474 nm] is also characteristic of the phenoxazone system.[6] On only this evidence a choice between these isomers is not possible, though the substitution pattern of the second (16) is hard to reconcile with that of the original aniline (1).



(16)

Phenoxazones are hydrolysed in mild alkali to 2-hydroxy-*N*-(2-hydroxyphenyl)-*p*-benzoquinone imines, a reaction which is instantly reversed by acid.[6,7] This property suggested a possible method for the chemical characterisation of the product, for if the ring-opening reaction was conducted in methanol with potassium methoxide, a possible pathway to a readily accessible *N*-phenyl-quinone imine (12) would be manifested (Scheme 2). Consideration of the method of preparation

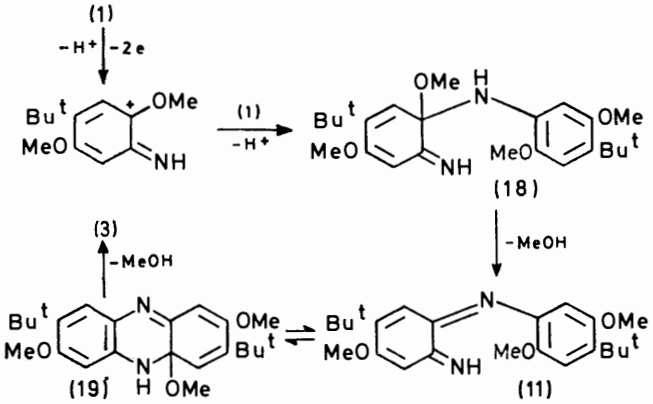


SCHEME 2

of phenoxazones from *o*-aminophenols and hydroxy-[6] or methoxy-quinones[7] suggested that isolation and independent synthesis of the intermediate quinone imine derived from (17) would be difficult, and the subsequent methylation step was therefore included. The reaction should thus yield (12) from (8), or the isomer if the phenoxazone were (16). Unfortunately, only a small quantity of dark brown gum was obtained, but this exhibited the same behaviour on t.l.c. as the synthetic quinone imine (12). This material and its isomer were readily prepared by acid-catalysed condensation of 2-methoxy-5-t-butyl-*p*-benzoquinone with 2,5-dimethoxy-4-t-butylaniline (1) and 2,4-dimethoxy-5-t-butylaniline, respectively. The phenoxazone was therefore considered to have structure (8), and this was confirmed by the synthesis to be described in Part III.

DISCUSSION

As was shown by t.l.c., the phenazine (3) was present in both oxidations of (1) prior to chromatography, and thus the di-imine (11), which must be intermediate in its formation, is able to undergo cyclisation at room temperature. The suggested sequence of reactions leading to the phenazine is shown in Scheme 3. This reaction contrasts with the behaviour of the dimethoxy-analogue of (11).[1] Thus, the presence of the *ortho*-methoxy-group on the phenyl portion of (11) greatly facilitates cyclisation. This has already been noted in connection with the oxidation of similarly substituted 2-anilinoanilines,[2] and is apparently a consequence of the ease of elimination of an alcohol or a hydrogen halide, resulting in the direct production of an aromatic system. Where no suitable leaving group is present, the immediate result of such a cyclisation is merely a dihydro-compound. A major factor influencing the cyclisation of compounds



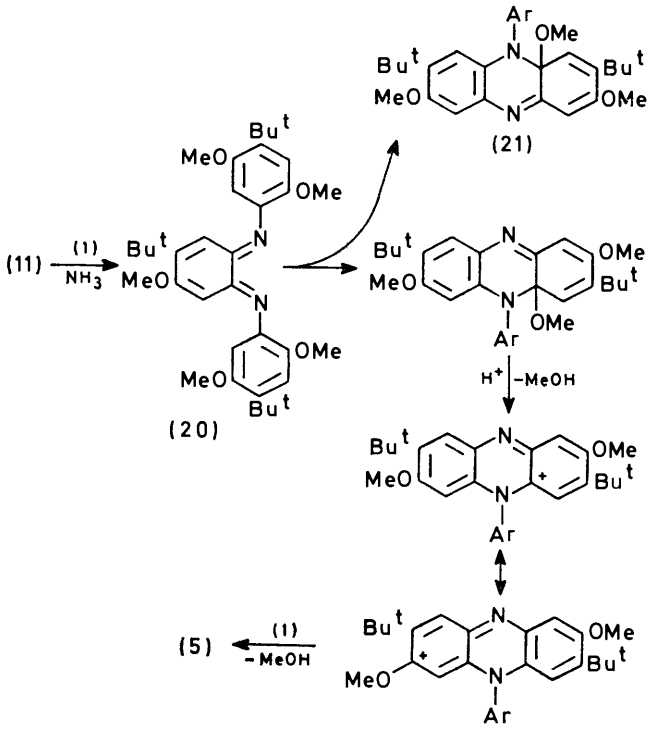
SCHEME 3

such as (11) may be electron release by the *ortho*-methoxy-group and this would certainly be so in an acid-catalysed reaction.

The di-imine (11) is also considered to be the precursor of compound (5) and of the quinone imine (6). Formation of the latter is easily explained as the result of addition of water to the di-imine (11) followed by loss of methanol. Compound (5) was only obtained from the ferricyanide oxidation, and this is ascribed to the presence of unchanged aniline (1), which could condense either with any of the quinone imine (10) that may have been produced in the oxidation, or with the di-imine (11) as shown in Scheme 4. In connection with the latter suggestion, if cyclisation of (20) occurs in the alternative

[5] J. F. Corbett, *Spectrochim. Acta*, 1965, **21**, 1411.
[6] W. Schäfer, *Progr. Org. Chem.*, 1964, **6**, 135.
[7] W. Schäfer and H. Schlude, *Tetrahedron Letters*, 1968, 2161.

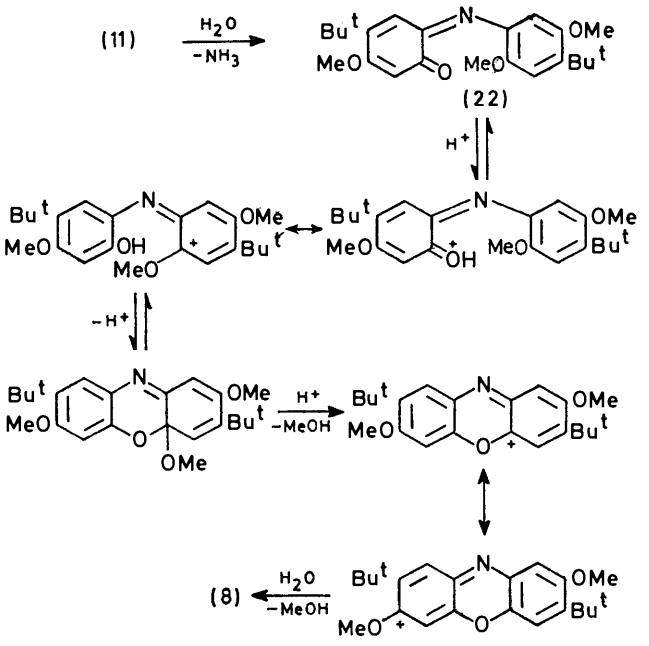
sense to give (21), in which the quaternary methoxy-group is not conjugated with any other methoxy-group, a second condensation with the aniline (1) will not produce compound (5).



Ar = 2,4-$(OMe)_2$-4-$Bu^tC_6H_2$

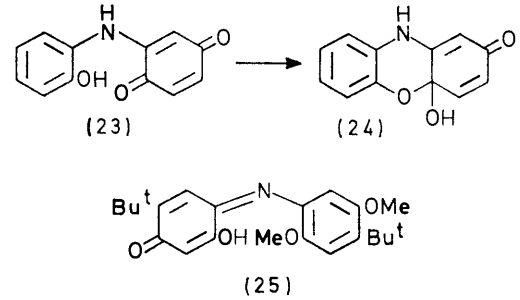
SCHEME 4

The only obvious precursor of the phenoxazone (8) appears to be the *N*-phenyl-*o*-quinone imine (22), which would result from hydrolysis of the di-imine (11). The suggested reaction sequence is shown in Scheme 5.

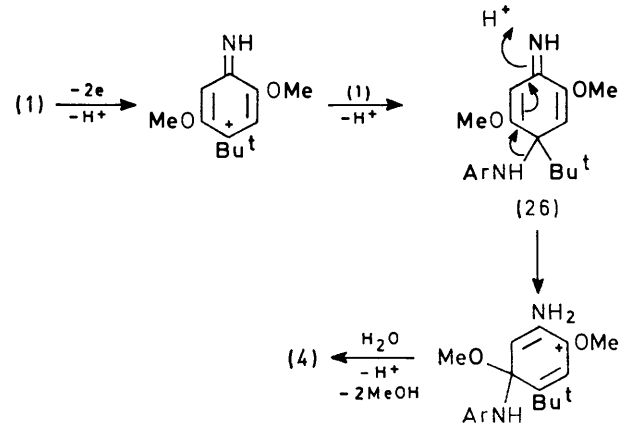


SCHEME 5

Ring closure of compounds such as (23), resulting from condensation of *o*-aminophenols with hydroxy-[6] or methoxy-quinones[7] to the hemiacetal (24), is formally analogous. The possibility of further hydrolysis of the *o*-quinone imine (22) to the *p*-quinone imine (25) and cyclisation of the latter to the phenoxazone must also be considered, but the failure of the amino-quinone imine (6) to cyclise under the conditions of its isolation indicates that this is an unlikely pathway.



The formation of the amino-quinone imine (4) during chromatography of the ferricyanide oxidation products parallels the formation of the related compound from 3-methoxy-4-t-butylaniline.[1] The suggested sequence is shown in Scheme 6, and again invokes preliminary *para* carbon–nitrogen coupling, followed by rearrangement of



Ar = 2,5-$(OMe)_2$-4-$Bu^tC_6H_2$

SCHEME 6

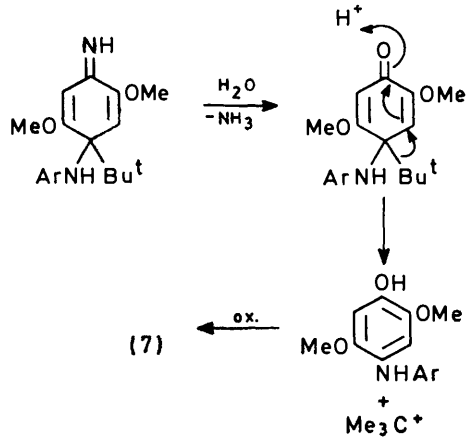
the iminocyclohexadiene (26) so produced. Whereas oxidation was subsequent to the hydration of the carbonium ion in the formation of the related compound from the monomethoxy-analogue, elimination of methanol is all that is required in the present case.

The isolation of the debutylated quinone imine (7) substantiates the assumptions made in both this and the previous paper concerning the involvement of imino-cyclohexadienes [*e.g.* (26)]. The least obscure pathway to (7) is shown in Scheme 7, and involves a type of debutylation for which there is ample precedent[8,9] in

[8] T. Matsuura and H. J. Cahnmann, *J. Amer. Chem. Soc.*, 1960, **82**, 2055.

[9] C. J. R. Adderley and F. R. Hewgill, *J. Chem. Soc.* (*C*), 1968, 1438.

the reactions of aryloxycyclohexadienones produced by the oxidative coupling of phenols.



Ar = 2,5-$(OMe)_2$-4-$Bu^tC_6H_2$

SCHEME 7

EXPERIMENTAL

General details were as described in the previous paper.[1] Light petroleum had b.p. 56—60°. 2,5-Dimethoxy-4-t-butylaniline (1), m.p. 84—85° (lit.,[10] 84—85°) was prepared as previously described. Its *acetate* crystallised as needles, m.p. 137·5—138·5° (from ether–light petroleum) (Found: C, 66·7; H, 8·35. $C_{19}H_{21}O_3$ requires C, 66·9; H, 8·4%).

Oxidation of 2,5-Dimethoxy-4-t-butylaniline (1).—(a) *By potassium ferricyanide.* The aniline (6·28 g) and oxidant (21·7 g) were treated as described for 3-methoxy-4-t-butylaniline,[1] and gave a dark crystalline residue. Removal of material soluble in light petroleum left *2,2′,5,5′-tetramethoxy-4,4′-di-t-butylazobenzene* (2) (640 mg) as orange plates, m.p. 243—245° (from chloroform–ether) (Found: C, 69·3; H, 8·3; N, 7·0. $C_{24}H_{34}N_2O_4$ requires C, 69·5; H, 8·3; N, 6·8%), $\lambda_{max.}$ ($CHCl_3$) 263, 328, 428, and 463sh nm (log ε 3·88, 3·73, 3·84, and 3·81), τ ($CDCl_3$) 2·72 (2 × ArH), 3·01 (2 × ArH), 5·96 (2 × OMe), 6·08 (2 × OMe), and 8·60 (2 × Bu^t). Chromatography of the light petroleum extract on alumina gave five fractions.

Fraction (i), eluted with light petroleum–ether (1 : 0 to 4 : 1), contained 3,8-dimethoxy-2,7-di-t-butylphenazine (3) (532 mg), m.p. and mixed m.p. 204—205°, and a small amount of the azobenzene (2).

Fraction (ii), eluted with light petroleum–ether (7 : 3 to 1 : 1) gave material which had a red fluorescence on t.l.c. plates under u.v. light. This was rechromatographed on silicic acid. Elution with light petroleum–ether (19 : 1) gave *8-methoxy-2,7-di-t-butyl-3H-phenoxazin-3-one* (8) (120 mg) as red needles, m.p. 124—126° (from light petroleum) (Found: C, 74·35; H, 7·4; N, 4·45. $C_{21}H_{25}NO_3$ requires C, 74·3; H, 7·4; N, 4·1%), $\nu_{max.}$ 1641m and 1613s cm^{-1}, $\lambda_{max.}$ (cyclohexane) 223, 263, 282sh, 346sh, 359, and 474 nm (log ε 4·13, 4·05, 3·51, 3·99, 4·03, and 4·19), τ (CCl_4) 2·87 (2H), 2·94 and 3·98 (2H), 6·07 (OMe), and 8·59 and 8·62 (2 × Bu^t). Rapid work was necessary during isolation of this material as it decomposed on chromatographic adsorbents to a red gum, which contained no methoxy-substituent (n.m.r.).

Fraction (iii), eluted with light petroleum–ether (1 : 1), deposited the aniline (1) from n-pentane. The mother liquors were chromatographed on silic acid. Elution with light petroleum–ether (7 : 3) gave a brownish red material, which was purified by preparative t.l.c. on alumina in benzene–hexane (1 : 1) to give *2-amino-4-(2,5-dimethoxy-4-t-butylphenylimino)-5-t-butylcyclohexa-2,5-dien-1-one* (4) (30 mg) as a brownish red gum, $\nu_{max.}$ 3496m, 3388m, 1661s, and 1631s cm^{-1}, τ ($CDCl_3$) 3·06 and 3·78 (2 × ArH), 3·47 and 4·19 (2 vinylic H), 5·67br (NH_2), 6·23 and 6·30 (2 × OMe), and 8·53 and 8·60 (2 × Bu^t).

Fraction (iv), eluted with ether, deposited crystals (1·88 g) of the aniline (1) from light petroleum. Chromatography of the mother liquors on alumina and elution with light petroleum–ether (9 : 1) gave *10,N-bis-(2,5-dimethoxy-4-t-butylphenyl)-7-methoxy-3,8-di-t-butyl-10H-phenazin-2-imine* (5) (109 mg) as blue needles, m.p. 182—183° (from light petroleum) (Found: C, 75·0; H, 8·5; N, 5·55. $C_{45}H_{59}N_3O_5$ requires C, 75·0; H, 8·2; N, 5·8%), $\lambda_{max.}$ (cyclohexane) 227, 307, and 570 nm (log ε 3·90, 3·79, and 4·09), τ (CCl_4) 2·87, 2·92, 3·11, 3·75, 3·91, and 4·92 (6H), 3·41 (2H), 6·07, 6·32, 6·37, 6·49, and 6·56 (5 × OMe), and 8·45, 8·63, 8·72, and 8·81 (4 × Bu^t).

Fraction (v), eluted with ether–chloroform (1 : 0 to 7 : 3) was separated from the aniline (1) and dark coloured materials by fractional crystallisation from light petroleum–ether. The first crops gave *4-(2,5-dimethoxy-4-t-butylphenylimino)-2,5-dimethoxycyclohexa-2,5-dien-1-one* (7) (10 mg) as pink needles, m.p. 207—209° (from ether–chloroform) (Found: C, 66·4; H, 7·15; N, 4·05. $C_{20}H_{25}NO_5$ requires C, 66·8; H, 7·0; N, 3·9%), $\nu_{max.}$ 1652s cm^{-1}, $\lambda_{max.}$ (cyclohexane) 213, 298, and 487 nm (log ε 4·29, 4·36, and 3·43), ($CDCl_3$) 3·07 and 3·54 (2 × ArH), 4·09 (2 vinylic H), 6·08, 6·23, 6·26, and 6·34 (4 × OMe), and 8·60 (Bu^t).

T.l.c. of a light petroleum solution of the oxidation product prior to chromatographic separation showed the phenazine (3) and the azobenzene (2) only. Yields of compounds (5) and (8) were variable.

(b) *By silver oxide.* The aniline (1) (6·28 g) was oxidised by silver oxide (16 g) in ether as described for 3-methoxy-4-t-butylaniline.[1] The dark crystalline residue was fractionated as in (a) to give the azobenzene (2) (860 mg), the phenazine (3) (1·97 g), the phenoxazone (8) (18 mg), and the quinone imine (7) (27 mg). In addition to these products, ether–chloroform (7 : 3) eluted material which was rechromatographed on alumina, and crystallised from ether–light petroleum as red needles (7 mg), m.p. 147·5—148·5°, of *5-amino-4-(2,5-dimethoxy-4-t-butylphenylimino)-2-t-butylcyclohexa-2,5-dien-1-one* (6) (Found: C, 71·4; H, 8·1; N, 7·6. $C_{22}H_{30}N_2O_3$ requires C, 71·3; H, 8·2; N, 7·6%), $\nu_{max.}$ 3497m, 3374m, 1646m, and 1623s cm^{-1}, $\lambda_{max.}$ (cyclohexane) 221, 296, and 470 nm (log ε 4·26, 4·26, and 3·54), τ ($CDCl_3$) 3·06 and 3·58 (2 × ArH), 3·42 and 4·34 (2 vinylic H), 4·73br (NH_2), 4·20 and 4·23 (2 × OMe), and 8·58 and 8·78 (2 × Bu^t).

T.l.c. prior to chromatographic separation of the oxidation products showed that the quinonoid products were formed during chromatography. None of the unchanged aniline (1) or the blue compound (5) could be detected. 4-Methoxy-5-t-butyl-1,2-benzoquinone was not formed in either oxidation.

2,2′,5,5′-Tetramethoxy-4,4′-di-t-butylazobenzene (3).—2,5-Dimethoxy-4-t-butylaniline (1) (210 mg) was diazotised in acetic acid and coupled with 4-methoxy-3-t-butylphenol. The resultant *2-hydroxy-2′,5,5′-trimethoxy-4,4′-di-t-butylazobenzene* (340 mg) crystallised as red-brown plates, m.p. 254—256° (from chloroform–ether) (Found: C, 68·6; H,

[10] F. R. Hewgill, *J. Chem. Soc.*, 1962, 4987.

8·35. $C_{23}H_{32}N_2O_4$ requires C, 69·0; H, 8·05%), τ ($CDCl_3$) 2·61, 2·68, 2·99 and 3·11 (4 × ArH), 5·97 (OMe), 6·02 (2 × OMe), and 8·57 and 8·58 (2 × Bu^t). With dimethyl sulphate and potassium carbonate in refluxing acetone during 18 h, the azophenol gave a tetramethoxyazobenzene identical with compound (2).

Condensation of 2,5-*Dimethoxy*-4-*t*-*butylaniline* (1).—(a) *With* 6-*imino*-4-*methoxy*-3-*t*-*butylcyclohexa*-2,4-*dien*-1-*one* (9). The *o*-quinone imine (9) [1] [from the parent aminophenol (390 mg)] was heated with the aniline (1) (400 mg) in acetic acid on a steam-bath for 3 min. Addition of water and extraction of the product with ether gave a deep red residue which deposited red needles (160 mg) from light petroleum. Recrystallisation from chloroform–ether gave 2-(2,5-*dimethoxy*-4-*t*-*butylanilino*)-4-(2,5-*dimethoxy*-4-*t*-*butylphenylimino*)-5-*t*-*butylcyclohexa*-2,5-*dien*-1-*one* (10), m.p. 225—227° (Found: C, 72·2; H, 8·2; N, 5·0. $C_{34}H_{46}N_2O_5$ requires C, 72·6; H, 8·2; N, 5·0%), $\nu_{max.}$ 3316m, 1653s, and 1628s cm^{-1}, τ ($CDCl_3$) 2·47br (NH), 3·10, 3·20, 3·52, and 3·71 (4H), 3·36 (2H), 6·18, 6·26, 6·31, and 6·56 (4 × OMe), and 8·49, 8·60, and 8·68 (3 × Bu^t).

Concentration of the light petroleum mother liquors gave unidentified orange-yellow crystals (54 mg) which decomposed at *ca.* 230° to a blue liquid. Chromatography of the residual mother liquors on alumina and elution with light petroleum–ether (1 : 0 to 4 : 1) gave material which was separated by preparative t.l.c. on silica gel in methanol–benzene (3 : 2) into two fractions. The first of these deposited crystals (8 mg) of 3,8-dimethoxy-2,7-di-t-butylphenazine (3), m.p. and mixed m.p. 204—205° (from light petroleum). The second fraction gave unidentified pale yellow needles (20 mg), m.p. 181—182°. More polar solvents eluted small amounts of the anilino-quinone imine (10), and then a deep brown gum (30 mg), identified as the amino-quinone imine (4) by i.r. spectroscopy after preparative t.l.c.

(b) *With the amino-quinone imine* (4) *and the anilino-quinone imine* (10). Reaction of the amino-quinone imine (4) with the aniline (1) in acetic acid during 7 h, dilution with water, and extraction with ether gave the anilino-quinone imine (10). The latter (10 mg) when treated with an excess of the aniline (1) in acetic acid during 6 h gave a blue product (3 mg) identical with the oxidation product (5) of the aniline (1).

(c) *With* 2-*amino*-5-*t*-*butyl*-1,4-*benzoquinone*. Reaction of the aniline (1) (209 mg) with this quinone (179 mg) in acetic acid for 5 h on a steam-bath gave a dark red solution. This was diluted with water and extracted with ether; the extract was evaporated and the residue was chromatographed on alumina. Elution with light petroleum–ether (1 : 0 to 4 : 1) gave the unchanged quinone (80 mg). Ether eluted material (60 mg) identical with the amino-quinone imine (6) obtained from the oxidation of the aniline (1).

(d) *With* 2,5-*dimethoxy*-1,4-*benzoquinone*. A solution of the aniline (1) (627 mg) and this quinone (504 mg) in acetic acid (30 ml) was heated on a steam-bath for 30 min. The purple solution was poured into water and the crystalline precipitate was filtered off and extracted with boiling ether to leave a residue of unchanged quinone. The extract was evaporated and the residue was fractionally crystallised from ether–light petroleum to give first 5-(or 2)-methoxy-2-(or 5)-2,5-dimethoxy-4-t-butylanilino)-4-(2,5-dimethoxy-4-t-butylphenylimino)cyclohexa-2,5-dien-1-one [(14) or (15)] (200 mg) as purple prisms, m.p. 212—214° (Found: C, 68·9; H, 7·6; N, 5·6. Calc. for $C_{31}H_{40}N_2O_6$: C, 69·4; H, 7·5; N, 5·2%), $\nu_{max.}$ 3307s, 1649s, and 1629m cm^{-1}, τ ($CDCl_3$) 3·15, 3·18, 3·33, 3·56, 3·73, and 4·03 (6H), 6·04, 6·20, and 6·53 (3 × OMe), 6·28 (2 × OMe), and 8·62 and 8·69 (2 × Bu^t). The more soluble component was 5-(2,5-*dimethoxy*-4-*t*-*butylanilino*)-2-*methoxy*-1,4-*benzoquinone* (13), obtained as purple needles (201 mg), m.p. 149—150° (Found: C, 66·3; H, 6·9; N, 4·4. $C_{19}H_{23}NO_5$ requires C, 66·1; H, 6·7; N, 4·1%), $\nu_{max.}$ 3320m, 1662s, and 1647sh cm^{-1}, τ ($CDCl_3$) 2·02 (NH), 3·08 and 3·10 (2 × ArH), 3·89 and 4·13 (2 vinylic H), 6·13 (2 × OMe), 6·18 (OMe), and 8·61 (Bu^t). T.l.c. of the mother liquors showed the presence of unchanged aniline (1), but not of the quinone imine (7).

(e) *With* 4-(2,5-*dimethoxy*-4-*t*-*butylphenylimino*)-2,5-*dimethoxycyclohexa*-2,5-*dien*-1-*one* (7). Addition of the aniline (1) (4 mg) in acetic acid (1·5 ml) to the quinone imine (7) (7 mg) in acetic acid (1·5 ml) at room temperature gave a deep blue solution. After 15 min this was poured into water. Extraction with ether and evaporation of the extract gave a purple residue, which was recrystallised from ether–light petroleum to give material (7 mg) identical with (14) or (15) obtained in (d).

(f) *With* 5-*methoxy*-2-*t*-*butyl*-1,4-*benzoquinone*. Equimolar solutions of the aniline (1) and the quinone in acetic acid were mixed and heated on a steam-bath for 15 min. The cooled solution was poured into water and extracted with ether. Evaporation of the extract and recrystallisation of the residue from ether–light petroleum gave 4-(2,5-*dimethoxy*-4-*t*-*butylphenylimino*)-5-*methoxy*-2-*t*-*butylcyclohexa*-2,5-*dien*-1-*one* (12) as dark reddish brown prisms, m.p. 108—109·5° (Found: C, 71·55; H, 7·8; N, 3·6. $C_{23}H_{31}NO_4$ requires C, 71·7; H, 8·1; N, 3·6%), $\nu_{max.}$ 1635s cm^{-1}, $\lambda_{max.}$ (cyclohexane) 218, 294, and 510 nm (log ε 4·04, 4·22, and 3·43), τ ($CDCl_3$) 3·14, 3·47, and 3·62 (3H), 4·30 (vinylic H), 6·20, 6·22, and 6·30 (3 × OMe), and 8·62 and 8·82 (2 × Bu^t).

Reactions of 8-*Methoxy*-2,7-*di*-*t*-*butyl*-3H-*phenoxazin*-3-*one* (8).—(a) *Reductive acetylation*. With zinc dust and sodium acetate in gently refluxing acetic anhydride the phenoxazone (8) gave, after 10 min, 3-*acetoxy*-10-*acetyl*-8-*methoxy*-2,7-*di*-*t*-*butylphenoxazine*, needles, softening at 94—100° to a viscous liquid (Found: C, 70·9; H, 7·5; N, 3·1. $C_{25}H_{31}NO_5$ requires C, 70·6; H, 7·3; N, 3·3%), $\nu_{max.}$ 1766s and 1691s cm^{-1}, τ (CCl_4) 2·62, 2·99, 3·04, and 3·25 (4 × ArH), 6·17 (OMe), 7·67 (2 × COMe), and 8·65 (2 × Bu^t).

(b) *Methylation*. The phenoxazone (8) (66 mg) was heated under gentle reflux for 4 h in dry methanol (14 ml) containing potassium methoxide (90 mg). The resulting deep blue mixture was cooled to 0°, then potassium carbonate (3 g) was added, followed by dimethyl sulphate, dropwise, until the evolution of carbon dioxide ceased. A further quantity (70 mg) of dimethyl sulphate was then added, and the mixture was heated under reflux for 5 h. After filtration the solution was evaporated to dryness under reduced pressure, leaving a brown gum. Application of this to alumina and elution with light petroleum–ether (7 : 3) gave *ca.* 3 mg of a brown-purple gum. This could not be purified without considerable loss, but the R_F values (t.l.c.) were identical with those of the quinone imine (12).

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