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

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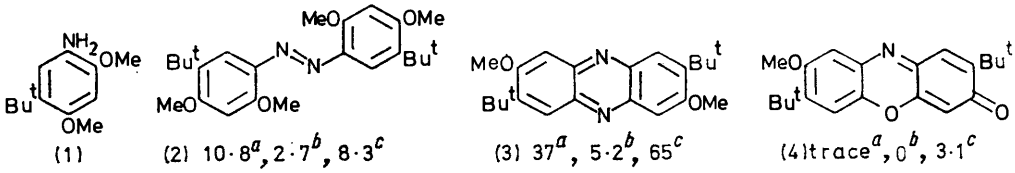
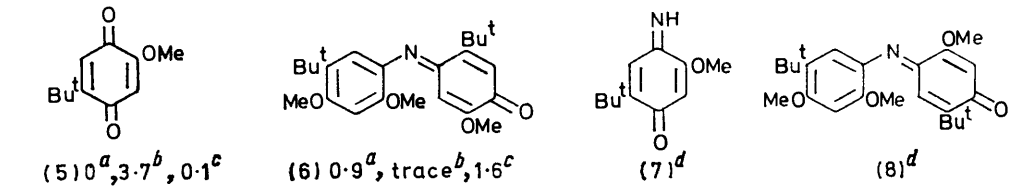
The oxidation of 2,4-dimethoxy-5-t-butylaniline (1) by silver oxide, and by potassium ferricyanide in sodium hydroxide and in sodium hydrogen carbonate, has been examined. Besides 2,2',4,4'-tetramethoxy-5,5'-di-t-butylazobenzene (2), a high yield of 3,8-dimethoxy-2,7-di-t-butylphenazine (3) and small quantities of 8-methoxy-2,7-di-t-butyl-3*H*-phenoxazin-3-one (4) result. The structure of the latter has been proved by synthesis from 2,5-dimethoxy-4-t-butylaniline and 4-methoxy-5-t-butyl-*o*-benzoquinone. Condensation of the latter quinone with (1) gives the isomeric phenoxazone (12). These reactions exemplify a new synthesis for phenoxazones. Other products isolated from the oxidation of the aniline (1) are the *p*-quinone (5), the quinone imine (7), and the two *N*-aryl-*p*-quinone imines (6) and (8).

CONSIDERATION of the mechanism of phenazine formation suggested in Part II of this series [1] indicates that the same phenazine (3) should also be obtained by oxidation of the isomeric aniline (1), unless *para*-carbon–nitrogen coupling becomes the dominant reaction. The expected *N*-phenyl-*o*-quinone di-imine intermediate might also give rise to the previously obtained [1] phenoxazone (4).

it was present as the hydrazone tautomer. Tautomerism of this kind has been noted previously,[2] and in the present case the hydrazone is presumably stabilised by hydrogen bonding to the *ortho*-methoxy-group, as 4-hydroxy-4'-methoxy-3,3'-di-t-butylazobenzene [3] showed no such tautomerism.

The *N*-phenyl-quinone imine (6) was shown by t.l.c. to be present before column chromatography. Its





[a] % Yield with $K_3Fe(CN)_6$–$NaHCO_3$. [b] % Yield with $K_3Fe(CN)_6$–NaOH. [c] % Yield with Ag_2O. [d] Additional products obtained with system *b* after oxidation for 2 h.

2,4-Dimethoxy-5-t-butylaniline (1) was prepared by nitration of 1,3-dimethoxy-4,6-di-t-butylbenzene, and reduction of the product. Unlike the other anilines studied, it proved very susceptible to autoxidation in alkaline solution. Although oxidation of the aniline (1) with potassium ferricyanide in aqueous sodium hydrogen carbonate gave a high yield of the phenazine (3), the expected phenoxazone was detectable in only trace amounts after chromatography of the oxidation mixture. The other major product was the azobenzene (2), which was identified spectrally and by synthesis [reaction of diazotised (1) with 5-methoxy-2-t-butylphenol, and methylation of the product]. The i.r. spectrum of the azophenol ($\nu_{max.}$ 3295 and 1601 cm^{-1}) indicated that, at least in dichloromethane solution, u.v. spectrum [$\lambda_{max.}$ 213, 290, and 520 nm (log ε 4·24, 4·15, and 3·49)] was very similar to that of the isomeric *N*-phenyl-quinone imine (8) [$\lambda_{max.}$ 213, 287, and 520 nm (log ε 4·08, 4·12, and 3·64)]. The quinonoid frequencies in the i.r. spectrum of (6) were 1662 and 1625 cm^{-1}, and for (8) 1641 and 1631 cm^{-1}, and show the previously noted [3] effect of an *ortho*-t-butyl group. Chemical evidence for the structure of (6) was obtained by acid hydrolysis to the known quinone (5).[4] The other hydrolysis product, the aniline (1), was not recovered, owing both to its rapid oxidation in air and to its reaction on alumina with the quinone (5) to give the isomeric *N*-phenyl-quinone imine (8). This reaction, as noted previously,[1] also occurred in acetic acid, and it thus reasonably establishes the structure of the

[1] Part II, R. K. Haynes and F. R. Hewgill, *J.C.S. Perkin I*, 1972, 408.

[2] H. Zollinger, 'Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds,' Interscience, New York, 1961, pp. 322 *et seq.*

[3] Part I, R. K. Haynes and F. R. Hewgill, *J.C.S. Perkin I*, 1972, 396.

[4] F. R. Hewgill, B. R. Kennedy, and D. Kilpin, *J. Chem. Soc.*, 1965, 2904.

oxidation product (6). Several other coloured products were formed in the ferricyanide–hydrogen carbonate oxidation, but could not be purified.

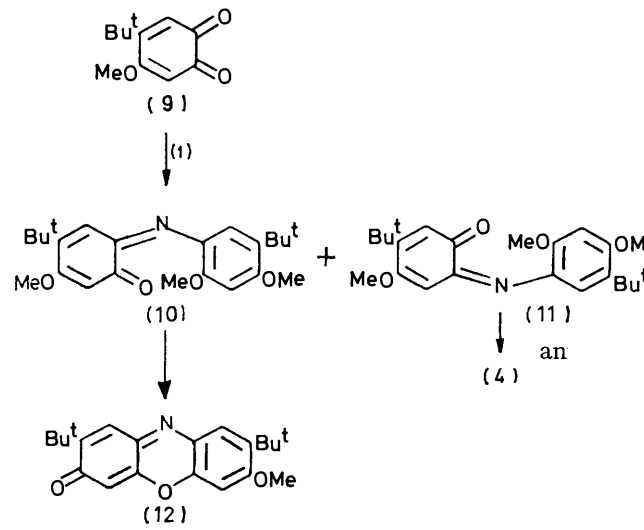
The use of ferricyanide in sodium hydroxide for the oxidation of (1) resulted in the formation of much polymeric material, and the yields of compounds (2) and (3) in particular were much reduced, whereas that of (5) was increased. Both compounds (5) and (6) were present before chromatography. When the oxidation was stopped after 2 h, two additional products, the *N*-phenyl-quinone imine (8), whose synthesis has already been described, and the quinone imine (7), were isolated. The latter was recognised by the presence of imine (3258 cm^{-1}) and quinone carbonyl (1642 cm^{-1}) i.r. absorption and the presence of n.m.r. signals due to two vinylic protons, and single methoxy- and t-butyl groups. It was also obtained in nearly quantitative yield by silver oxide oxidation of the *p*-aminophenol prepared by reduction of the nitrosation product of 5-methoxy-2-t-butylphenol. The *N*-phenylquinone imine (8) was not present before chromatography, and undoubtedly arose by the alumina-catalysed condensation of unchanged (1) with either the quinone imine (7) or the quinone (5).

The silver oxide oxidation of the aniline (1) was notable in that the phenazine (3) was produced in very high yield (65%). Compounds (2), (4), (5), and (6) were also isolated. Although the presence of the quinone (5) prior to chromatography could not be established because of the presence of coloured materials with similar R_F values, the quinone imine (6) was clearly evident.

DISCUSSION

The formation of the phenazine (3) and of the phenoxazone (4) obviously parallels their formation from the isomeric aniline, 2,5-di-methoxy-4-t-butylaniline [1] (13). In this case it is the methoxy-group originally on the phenyl ring of the di-imine that is eliminated during formation of the phenoxazone.

Although the *o*-quinone (9) could not be detected in the oxidation of either (1) or its isomer, 2,5-dimethoxy-4-t-butylaniline (13), the reaction of this quinone with these anilines to produce the respective *N*-phenyl-*o*-quinone imine intermediates, (10) and (14), may conceivably have occurred during the oxidation, and thus the observation that the phenoxazone (4) was formed during chromatography could still be explained by the alumina-induced cyclisation of the respective intermediates. However, the formation of quinone imines such as (11) by reaction of the aniline at the carbonyl group conjugated with the methoxy-group of the quinone (9) appears unlikely, as this quinone reacts with 2,4-dinitrophenylhydrazine almost exclusively at the carbonyl group conjugated with the t-butyl group.[5] However, there remains the possibility that the *N*-phenyl-*o*-quinone imine (10) derived from (1) could cyclise to the isomeric phenoxazone (12) as shown in Scheme 1.



SCHEME 1

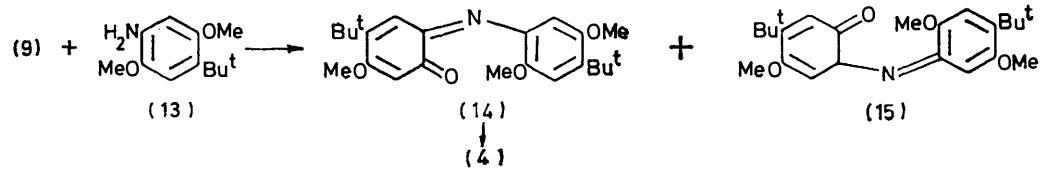
Accordingly, the aniline (1) was treated with the quinone (9) in aqueous acetic acid. Two highly coloured products were isolated, one only in trace amounts. This was shown by t.l.c. to be the phenoxazone (4). The major product (78% yield) was the predicted one, the phenoxazone (12). The u.v. spectrum of this ($\lambda_{max.}$ 228, 255, 385, and 460 nm) was similar to that of compound (4), but the i.r. spectrum showed only a single strong quinonoid band, at 1613 cm^{-1}. The n.m.r. spectrum, with signals from four non-coupled ring protons, one methoxy-group, and two t-butyl groups was consistent with structure (12). Reductive acetylation gave a diacetate which had both *o*-acetyl and tertiary amide absorptions in its i.r. spectrum.

The acid-catalysed condensation of the isomeric aniline (13) with the *o*-quinone (9) was also successful, and in this case the only phenoxazone formed was (4), in a yield of 68%. This result unequivocally establishes the structure of compound (4), for, as can be seen in Scheme 2, if the predominant reaction had occurred at the carbonyl group *para* to the t-butyl group of the quinone (9), the resultant *N*-phenyl-*o*-quinone imine (15), having no methoxy-group *para* to the nitrogen atom, could not form a phenoxazone.

The absence of the phenoxazone (12) among the oxidation products of the aniline (1) shows that the *o*-quinone (9) is not a precursor of the phenoxazone (4) obtained from the oxidations of this, and consequently, of the isomeric aniline (13), and thus indirectly supports the suggestions made in the previous paper [1] concerning the origin of the phenoxazone (4). The condensations shown in Schemes 1 and 2 represent a synthesis of possible value for the preparation of phenoxazones, providing that the starting materials have the substitution patterns necessary for the cyclisation and subsequent hydrolytic processes. However, the marked

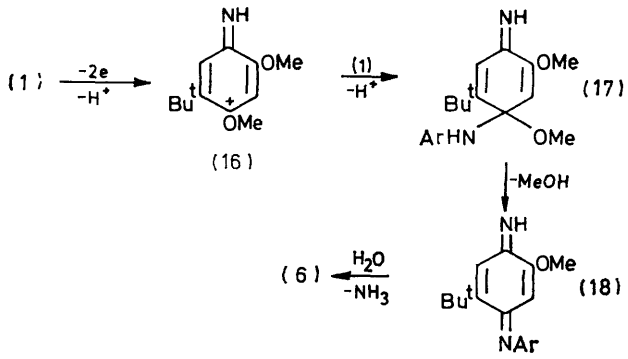
[5] F. R. Hewgill, *J. Chem. Soc.*, 1962, 4987.

tendency of lightly substituted *o*-quinones to undergo 1,4- rather than 1,2-addition appears to limit the application to *o*-quinones with blocking substituents such as alkyl groups in the 4- or 5-positions.



SCHEME 2

As regards the uncyclised oxidation products, the formation of the *N*-phenyl-*p*-quinone imine (6) appears

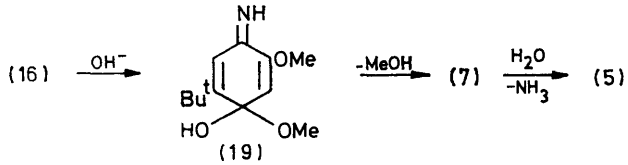


Ar = 2,4-$(OMe)_2$-5-$Bu^tC_6H_2$

SCHEME 3

straightforward, and by analogy with the oxidation of *p*-anisidine,[6] is considered to proceed *via* the *N*-phenyl-*p*-quinone di-imine (18), as in Scheme 3. This intermediate is then hydrolysed, either by the reaction medium or subsequent chromatography, to the imine (6).

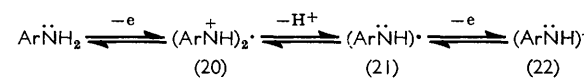
The very low yield of compound (6) obtained from the ferricyanide–sodium hydroxide oxidation of (1) is of interest. The other quinonoid products of this oxidation [apart from the *N*-phenyl-quinone imine (8), whose origin has already been discussed], that is, the quinone (5) and its precursor the quinone imine (7), are not derived by hydrolysis of the *N*-phenyl-quinone imine (6) or the di-imine (18) *in situ* or on alumina, as compound (6) was unaffected by chromatography or boiling methanolic alkali. This indicates that the



SCHEME 4

carbonium ion (16) is predominantly hydroxylated under the oxidation conditions to give the imino-quinol (19) (Scheme 4). Elimination of methanol would then produce the quinone imine (7), which was shown to be partly converted on alumina into the quinone (5). This process finds analogy in the oxidative demethylation of methoxyphenols, in which oxidation of the aryloxy-radical to a carbonium ion, with subsequent hydration and elimination of methanol, has been proposed in certain cases.[4] On the other hand, quinones also result from the hydrolysis of acid-sensitive aryloxycyclohexadienones, formed by the coupling of aryloxy-radicals. However, it is unlikely that the latter process can be extended to the present case, for it is unreasonable to suppose that the intermediate most closely related to these dienones, the iminocyclohexadiene (17), should suffer acid-catalysed hydrolysis to a significant extent only in the most alkaline medium used.

The isolation of compound (7) is thus of particular significance in relation to the species involved in the oxidative coupling of anilines, for which there are more possibilities than is the case with phenols.[8] The most obvious of these are represented in Scheme 5. In the



SCHEME 5

anilinium radical cation (20), which has been regarded as a possible dimerising species,[6] consideration of resonance structures shows that the unpaired electron may be delocalised to the *ortho* and *para* ring carbon atoms, but the positive charge to only the 1-, 3-, and 5-positions. There is thus no opportunity for hydroxylation at the *para*-position. By analogy with aryloxy-radicals, which are not hydroxylated under conditions of ferricyanide oxidation, the anilino-radical (21) is also unlikely to be hydroxylated. This leaves the nitrenium cation (22) as the most likely precursor of the quinone imine (7), by the route shown in Scheme 4. This cation (22) could be produced by either disproportionation or further oxidation of the anilino-radical (21). As pointed out by Daniels and Saunders,[9] electrophilic substitution of unoxidised aniline by the cation (22) can satisfactorily account for all the observed products. Furthermore, in the three amines studied, a cationic process is more in accord with the decreasing yields of azobenzenes, and the increasing

[6] J. Bacon and R. N. Adams, *J. Amer. Chem. Soc.*, 1968, **90**, 6596.

[7] C. J. R. Adderley and F. R. Hewgill, *J. Chem. Soc.* (*C*), 1968, 1434.

[8] D. H. R. Barton, *Chem. in Britain*, 1967, 330.

[9] D. G. H. Daniels and B. C. Saunders, *J. Chem. Soc.*, 1951, 2112.

yields of the phenazine (3) in passing from 3-methoxy-4-t-butylaniline to 2,5-dimethoxy-4-t-butylaniline to 2,4-dimethoxy-5-t-butylaniline, the expected order of increasing basicity. Thus at this stage of the investigation, some evidence has been obtained for the intermediacy of cations such as (22), but none for neutral anilino-radicals.

EXPERIMENTAL

General details were as described in Part I.[3] Light petroleum had b.p. 56—60°.

2,4-Dimethoxy-5-t-butylaniline (1).—Dropwise addition of nitric acid (35%; 50 ml) to a stirred solution of 1,3-dimethoxy-4,6-di-t-butylbenzene (25 g) in acetic acid (250 ml) and acetic anhydride (75 ml) at −5° during 1·3 h gave, after dilution and crystallisation from methanol, 2,4-dimethoxy-5-t-butylnitrobenzene (22 g, 92%), m.p. 102—103·5° (lit.,[10] 101—102°). This was hydrogenated in ether over palladium–charcoal (10%) to give a quantitative yield of *2,4-dimethoxy-5-t-butylaniline* (1), as fine needles, m.p. 71·5—72·5° (from light petroleum) (Found: C, 68·8; H, 9·0; N, 6·6. $C_{12}H_{19}NO_2$ requires C, 68·9; H, 9·15; N, 6·7%), τ 3·51 and 3·66 (2 × ArH), 6·23 and 6·25 (2 × OMe), 6·72 (NH_2), and 8·72 (Bu^t). The *acetamide* crystallised as needles, m.p. 134—135° (from ether–light petroleum) (Found: C, 66·6; H, 8·1. $C_{14}H_{21}NO_3$ requires C, 66·9; H, 8·4%).

Oxidation of 2,4-*Dimethoxy-5-t-butylaniline* (1).—(a) *By potassium ferricyanide.* The aniline (1) (6·28 g) was oxidised by potassium ferricyanide (21·7 g) as described in Part I,[3] except that sodium hydrogen carbonate (3·3 g) was used instead of sodium hydroxide. Deoxygenated solutions were used throughout. The reaction mixture yielded a dark residue which, after extraction with light petroleum and crystallisation from ether, then chloroform, gave *2,2′,4,4′-tetramethoxy-5,5′-di-t-butylazobenzene* (2) (540 mg) as long orange prisms, m.p. 262—263° (Found: C, 69·2; H, 8·0; N, 6·9. $C_{24}H_{34}N_2O_4$ requires C, 69·5; H, 8·3; N, 6·8%), $\lambda_{max.}$ ($CHCl_3$) 265, 338, 415, and 442sh nm (log ε 3·97, 3·79, 3·83, and 3·77), τ ($CDCl_3$) 2·81 (2 × ArH), 3·44 (2 × ArH), 5·97 (2 × OMe), 6·08 (2 × OMe), and 8·62 (2 × Bu^t).

The light petroleum extracts were chromatographed on alumina to give four main fractions. Fraction (i), eluted with light petroleum–ether (1 : 0 to 4 : 1) consisted of 3,8-dimethoxy-2,7-di-t-butylphenazine (3) (1·98 g), m.p. and mixed m.p. 204—205°. Fraction (ii), eluted with light petroleum–ether (4 : 1) gave more of the azobenzene (2) (130 mg). The mother liquors were combined with fraction (iii), eluted by light petroleum–ether (7 : 3), and fractionated on silicic acid to give two main bands. The first (*ca.* 1 mg), eluted by light petroleum–ether (19 : 1), was shown by t.l.c. to contain the phenoxazone (4) and a trace of unchanged aniline (1). The second gave small amounts of the azobenzene (2) and then 4-(2,4-*dimethoxy*-5-*t-butylphenylimino*)-2-*methoxy*-5-*t-butylcyclohexa*-2,5-*dien*-1-*one* (6) (54 mg) as purple prisms, m.p. 141·5—142·5° (from benzene) (Found: C, 71·9; H, 7·9; N, 3·9. $C_{23}H_{31}NO_4$ requires C, 71·7; H, 8·1; N, 3·6%), $\nu_{max.}$ 1662s and 1625s cm^{-1}, $\lambda_{max.}$ (cyclohexane) 213, 290, and 520 nm (log ε 4·24, 4·15, and 3·49), τ ($CDCl_3$) 3·44 (2 × ArH), 3·69, and 3·96 (2 vinylic H), 6·10, 6·21, and 6·46 (3 × OMe), 8·53, and 8·65 (2 × Bu^t). Fraction (iv), eluted by light petroleum–ether (7 : 3 to 0 : 1) gave a deep red gum (110 mg) which could not be adequately separated by chromatography.

When sodium hydroxide (3·6 g) was used in place of sodium hydrogen carbonate, the petroleum-insoluble portion of the residue included dark polymeric material as well as the azobenzene (2) (165 mg). Chromatography of the petroleum-soluble fraction on alumina and elution with light petroleum (b.p. 35—45°) gave a pale yellow band which deposited crystals (150 mg) of 2-methoxy-5-t-butyl-1,4-benzoquinone (5), m.p. and mixed m.p. with an authentic sample 161—162°. From the mother liquors the phenazine (3) (276 mg), more of the quinone (5) (50 mg), and a trace of the quinone imine (6) were obtained.

When the reaction mixture containing sodium hydroxide was processed 2 h after the addition of ferricyanide, chromatography on alumina gave two additional products. The first, eluted by light petroleum–ether (9 : 1) was *4-imino-5-methoxy-2-t-butylcyclohexa-2,5-dien-1-one* (7) (12 mg), pale yellow plates, m.p. 151—152° (from ether–light petroleum) (Found: C, 68·1; H, 7·7; N, 7·1. $C_{11}H_{15}NO_2$ requires C, 68·4; H, 7·8; N, 7·25%), $\nu_{max.}$ 3258m and 1642s cm^{-1}, τ (CCl_4) 3·03 and 4·35 (2 vinylic H), 6·18 (OMe), and 8·69 (Bu^t). The second, eluted by light petroleum–ether (4 : 1) was 4-(2,4-*dimethoxy-5-t-butylphenylimino*)-5-*methoxy*-2-*t-butylcyclohexa*-2,5-*dien*-1-*one* (8) (18 mg), dark red needles, m.p. 177—179° (from ether) (Found: C, 71·5; H, 8·2; N, 3·8. $C_{11}H_{15}NO_2$ requires C, 71·7; H, 8·1; N, 3·6%), $\nu_{max.}$ 1641s and 1631s cm^{-1}, $\lambda_{max.}$ (cyclohexane) 213, 287, and 520 nm (log ε 4·08, 4·12, and 3·64), τ ($CDCl_3$) 3·34 and 3·38 (2 × ArH), 3·49, and 4·30 (2 vinylic H), 6·10, 6·18, and 6·23 (3 × OMe), and 8·81 (2 × Bu^t). T.l.c., which demonstrated the absence of this material prior to chromatography, did not reveal the presence of 4-methoxy-5-t-butyl-1,2-benzoquinone in this or any of the preceding or following oxidations.

(b) *By silver oxide.* With this oxidant (16 g) in ether, the aniline (1) (6·28 g) gave after 12 h a deep red solution. The same methods of product isolation gave the azobenzene (2) (516 mg), the phenazine (3) (3·44 g), the quinone (5) (7 mg), the phenoxazone (4) (155 mg), and the quinone imine (6) (93 mg).

2,2′,4,4′-Tetramethoxy-5,5′-di-t-butylazobenzene (2).—Addition of the diazotised aniline (1) to an alkaline solution of 5-methoxy-2-t-butylphenol gave 4-hydroxy-5,5′-di-t-butyl-2,2′,4′-trimethoxyazobenzene as red needles, m.p. 177—179° (from chloroform) (Found: C, 68·6; H, 8·0. $C_{23}H_{32}N_2O_4$ requires C, 69·0; H, 8·05%), $\nu_{max.}$ (CH_2Cl_2) 3295m and 1601s cm^{-1}, τ ($CDCl_3$) 2·38, 2·71, 3·50, and 3·85br (4 × ArH), and 8·60 (Bu^t). Methylation with dimethyl sulphate and potassium carbonate in refluxing acetone gave the tetramethoxyazobenzene (2), identical with the oxidation product.

Hydrolysis of 4-(2,4-*Dimethoxy*-5-*t-butylphenylimino*)-2-*methoxy*-5-*t-butylcyclohexa*-2,5-*dien*-1-*one* (6).—The quinone imine (6) (86 mg) was heated under reflux in methanol (20 ml) containing hydrochloric acid (0·3 ml) for 2 h. The cooled solution was neutralised with sodium hydrogen carbonate, and the methanol was removed under reduced pressure. The residue was extracted with ether, the extract was evaporated, and the residue was chromatographed on silicic acid. Light petroleum–ether (19 : 1) eluted 2-methoxy-5-t-butyl-1,4-benzoquinone (5) (15 mg), and light petroleum–ether (9 : 1) eluted the quinone imine (8) (9 mg). The quinone

[10] M. S. Carpenter, W. M. Easter, and T. F. Wood, *J. Org. Chem.*, 1951, **16**, 586.

imine (6) was recovered unchanged after attempted hydrolysis in methanolic aqueous sodium hydroxide for 20 h.

4-Imino-5-methoxy-2-t-butylcyclohexa-2,5-dien-1-one.—Sodium nitrite (64 mg) in water (2 ml) was added dropwise to an ice-cold solution of 5-methoxy-2-t-butylphenol (135 mg) in acetic acid (8 ml) containing water (0·5 ml). A bulky yellow-green precipitate formed towards the end of the addition. After addition of water (30 ml) the product was filtered off and crystallised from methanol to give *5-methoxy-4-nitroso-2-t-butylphenol* (104 mg) as plates, m.p. 205—207° (Found: C, 63·2; H, 7·3. $C_{11}H_{15}NO_3$ requires C, 63·1; H, 7·2%), $\nu_{max.}$ (CH_2Cl_2) 3529m, 3201br,m, 1628, and 1576s cm^{-1}, τ ($CDCl_3$) 2·51 and 4·26 (2 × ArH), 6·17 (OMe), and 8·68 (Bu^t). Reduction of the nitroso-compound with sodium dithionite gave *4-amino-5-methoxy-2-t-butylphenol* (70%), needles, m.p. 170—172° (decomp.) (from ether) (Found: C, 67·8; H, 8·6. $C_{11}H_{17}NO_2$ requires C, 67·7; H, 8·9%). The *triacetate* crystallised as needles, m.p. 133—134° (from ether), τ ($CDCl_3$) 7·65 (COMe) and 7·73 (2 × COMe).

This amino-phenol (38 mg) was shaken for 30 min with silver oxide and anhydrous sodium sulphate in ether (10 ml). After filtration the ether was evaporated off under reduced pressure to leave a pale yellow crystalline residue (33 mg), which deposited yellow plates (from ether) of the imine (7).

With zinc dust and sodium acetate in refluxing acetic anhydride, the imine after 5 min gave a triacetate identical with that obtained from the parent amino-phenol.

Condensation of 2-Methoxy-5-t-butyl-1,4-benzoquinone (5) *with 2,4-Dimethoxy-5-t-butylaniline* (1).—When acetic acid solutions containing equimolar quantities of the quinone (5) and the aniline (1) were mixed, the solution became red. After being heated for 15 min on a steam-bath, the solution was cooled, poured into water, and extracted with ether. Evaporation of the extract and recrystallisation of the residue gave 4-(2,4-dimethoxy-5-t-butylphenylimino)-5-methoxy-2-t-butylcyclohexa-2,5-dien-1-one (8), identical with the oxidation product.

Condensation of 5-Methoxy-4-t-butyl-1,2-benzoquinone (9).—(a) *With 2,4-dimethoxy-5-butylaniline* (1). Addition of the aniline (1) (209 mg) in aqueous acetic acid (90%; 10 ml) to the *o*-quinone (9) (194 mg) in the same solvent (10 ml) gave a deep red solution. After being heated for 2 h on a steam-bath, the solution was cooled, poured into water, and extracted with ether. The washed extract was evaporated to leave an orange-red residue (265 mg). Crystallisation from light petroleum gave *7-methoxy-2,8-di-t-butyl-3H-phenoxazin-3-one* (12) as orange-red prisms, m.p. 199—201° (Found: C, 74·15; H, 7·5; N, 4·2. $C_{21}H_{25}NO_3$ requires C, 74·3; H, 7·4; N, 4·1%), $\nu_{max.}$ 1613s cm^{-1}, $\lambda_{max.}$ (cyclohexane) 228, 255, 272, 283, 368sh, 385, and 460 nm (log ε 4·24, 4·03, 3·89, 3·76, 3·86, 3·91, and 4·27), τ ($CDCl_3$) 2·36, 2·70, 3·22, and 3·78 (4H), 6·04 (OMe), and 8·57 (2 × Bu^t). The only other product was a trace of the isomeric phenoxazone (4), detected in the mother liquors by t.l.c.

Reductive acetylation of the phenoxazone (12) gave *3-acetoxy-10-acetyl-7-methoxy-2,8-di-t-butylphenoxazine* as plates (from light petroleum) softening between 76 and 86°, then partially resolidifying, softening again at 113°, and finally melting at 135° (Found: C, 70·8; H, 7·35. $C_{25}H_{31}NO_5$ requires C, 70·6; H, 7·3%), $\nu_{max.}$ 1762s and 1680s cm^{-1}, τ (CCl_4) 2·47, 2·79, 3·28, and 3·41 (4 × ArH), 6·16 (OMe), 7·71 and 7·76 (2 × COMe), and 8·64 (2 × Bu^t).

(b) *With 2,5-dimethoxy-4-t-butylaniline* (13). Treatment of the aniline (13) (209 mg) with the quinone (9) (194 mg) under the same conditions as in (a) gave, after 2·2 h, a brown-red gum. Chromatography on alumina and elution with light petroleum–ether (9 : 1) gave the isomeric phenoxazone (4) (230 mg), identical with the material obtained by oxidation. More polar solvents eluted a brown gum which was not further investigated.

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