Amine Oxidation and the Chemistry of Quinone Imines. Part I. 3-Methoxy-4-t-butylaniline

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With potassium ferricyanide or silver oxide the oxidation of 3-methoxy-4-t-butylaniline gives an azobenzene (4) and three phenazines (5)—(7). Chromatographic separation of the ferricyanide oxidation products on neutral alumina results in the formation of *N*-aryl-*p*-quinone imines (8) and (9), the *NN'*-diaryl-*p*-quinone di-imine (10), and an *N*-arylphenazineimine (11). With the exception of compounds (8) and (10) these products are also formed during chromatography of the silver oxide oxidation products, in which the presence of the *N*-aryl-*o*-quinone di-imine (27) is disclosed. The latter is shown to be the precursor of the quinone imines (9) and (11).

Chemical and spectroscopic evidence is advanced for the structures of these products, and their likely origin is demonstrated. The intermediacy and subsequent rearrangement of an iminocyclohexadiene oxidation product (34) can explain the formation of the quinone imine products (8) and (10). No carbon–carbon coupled products were isolated.

In striking contrast to the oxidation of phenols, products arising from carbon–carbon coupling have almost never been isolated from the oxidation of anilines; the only exception known to us is the formation of benzidine in the anodic oxidation of aniline at low pH.[1] Nevertheless, such coupling does sometimes occur in the oxidation of secondary and tertiary amines.[2-4] The only com-

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

[2] R. F. Bridger, D. A. Law, D. F. Bowman, B. S. Middleton, and K. U. Ingold, *J. Org. Chem.*, 1968, **33**, 4329; R. F. Bridger, *ibid.*, 1970, **35**, 1746.

[3] D. F. Bowman, B. S. Middleton, and K. U. Ingold, *J. Org. Chem.*, 1969, **34**, 3456.

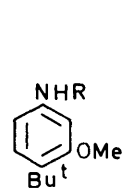
[4] W. L. Carrick, G. L. Karapinka, and G. T. Kwiatkowski, *J. Org. Chem.*, 1969, **34**, 2388.

prehensive study in terms of product analysis is that of Saunders and his co-workers [5] on the peroxidase-catalysed oxidation of various anilines by hydrogen peroxide, and by Fenton's reagent. In spite of much speculation there is no compelling evidence that anilino-radicals or radical cations are involved in the formation of the typical products, namely azobenzenes, phenazines, and quinone imines, of these and related oxidations. By use of a rapid flow system Fox and Waters [6] succeeded in obtaining e.s.r. spectra of arylammonium radical cations produced by oxidation of various anilines with cerium(IV) sulphate, but signals could only be obtained if powerful electron-withdrawing substituents were present.

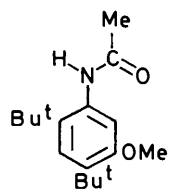
In this and the following two papers we examine in detail the oxidation products of three amines, selected primarily for their relationship to phenols which have given high yields of di- and tri-meric oxidation products.[7,8] Numerous reagents have been used to oxidise anilines, chiefly to azobenzenes, and, as is the case with manganese dioxide, sometimes in high yields, but we have confined our studies to the action of potassium ferricyanide and silver oxide, which are perhaps the best reagents for phenolic oxidative coupling, in the hope of isolating carbon–carbon coupled products.

The first amine studied was 3-methoxy-4-t-butylaniline (1), in which possible carbon–carbon coupling should be confined to the 6-position. This was prepared by the alkylation of *N*-acetyl-*m*-anisidine with t-butyl chloride and a zinc chloride catalyst, giving a mixture of products from which (2) was obtained in good yield. As the n.m.r. spectrum of (2), while showing 1,2,4-substitution, does not exclude the *o*-t-butylacetanilide alternative, we also prepared compound (1) by oxidation of 3-methoxy-4-t-butyltoluene to 3-methoxy-4-t-butylbenzoic acid, followed by the Curtius reaction. Acetylation of the resultant aniline gave material identical with our original sample of (2).

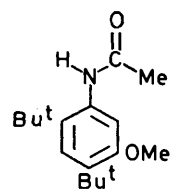
Consideration of the n.m.r. spectrum of the other major product of the t-butylation, the di-t-butyl compound (3) also enables a distinction to be made between (2) and the alternative *o*-t-butyl isomer. In this spectrum [τ ($CDCl_3$) 2·62 (NH), 2·74 and 2·97 (ArH), 6·24 (OMe), 7·83 and 8·08 (NAc), and 8·62 (2 × Bu^t)], the



(1) R = H
(2) R = Ac



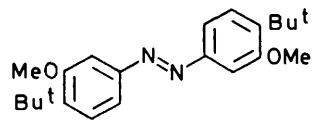
(3a)



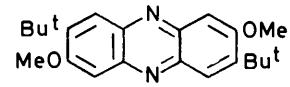
(3b)

CH_3·CO·N resonances at τ 7·83 and 8·08 occur in the intensity ratio 2·5 : 0·05. The latter signal, in the light of recent work on rotational isomerism in substituted acetanilides,[9] is assigned to that configuration in which the methyl protons of the acetamido-group lie within the shielding zone of the benzene ring. In this, the *exo*-isomer (3b), the aromatic protons are assumed to have a coincidental chemical shift at τ 2·74, as this accounts for a disparity in the integral ratio (1·16 : 0·84) of the signals at τ 2·74 and 2·97. Apparently substitution by a t-butyl group *ortho* to the acetamido-substituent partially stabilises the *exo*-isomer (3b) with respect to the ' normal ' *endo*-isomer (3a). Thus, in the spectrum of (2) [τ (Ac) 7·77] the absence of CH_3·CO·N resonances at high field is an indication that the t-butyl group is *para* to the acetamido-group.

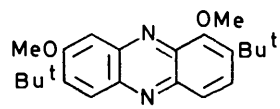
By oxidation of the aniline (1) with excess of alkaline potassium ferricyanide or silver oxide followed by chromatography we obtained compounds (4)—(11) in the



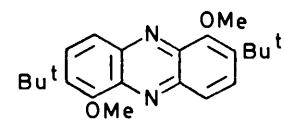
(4) 26.40



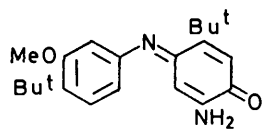
(5) 1·7, 2·4



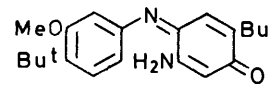
(6) 0·4, 0·7



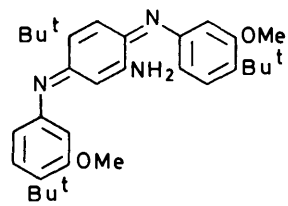
(7) trace amounts



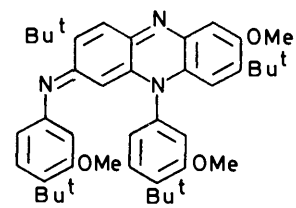
(8) 3·1, 0



(9) 2·5, 7·9



(10) 0·4, 0



(11) 3·0, 1·8

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

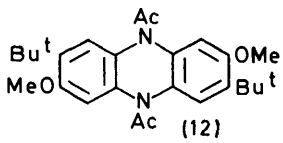
yields indicated. Extensive chromatographic fractionation was necessary for the isolation of these products, and was hindered by the presence of unchanged aniline in the ferricyanide product. By t.l.c. it was demonstrated that the azobenzene (4) and the three phenazines (5)—(7) were the only identifiable products present prior to column chromatography, compounds (8)—(11) being artifacts. No carbon–carbon coupling appears to have

[5] B. C. Saunders, A. G. Holmes-Seidle, and B. P. Stark, ' Peroxidase,' Butterworths, London, 1964.
[6] W. M. Fox and W. A. Waters, *J. Chem. Soc.*, 1964, 6010.
[7] C. J. R. Adderley and F. R. Hewgill, *J. Chem. Soc.* (*C*), 1968, 1438.
[8] F. R. Hewgill, *J. Chem. Soc.*, 1962, 4987.
[9] J. P. Chupp and J. F. Olin, *J. Org. Chem.*, 1967, **32**, 2297.

taken place, but the results are of interest in their bearing on the mechanism of phenazine formation.

Product Identification.—The structures assigned to the products rest on the following evidence. The major and most easily isolated product, the azobenzene (4), was cleaved by reductive acetylation to 3-methoxy-4-t-butylacetanilide (2). Its u.v. spectrum resembled that of 4,4′-dimethoxy-3,3′-di-t-butylazobenzene, and those of other azobenzenes.[10,11]

The symmetrical nature of the phenazine (5) is clear from its n.m.r. spectrum, in which the two pairs of like aromatic protons appear as two singlets, as do the methoxy- and t-butyl groups. Reductive acetylation gave the equally symmetrical diamide (12). The u.v. spectrum of (5) was characteristic of a phenazine [12,13] rather than of the alternative benzo[*c*]cinnoline.[12] Compound (5) was independently synthesised by heating 2-bromo-4-methoxy-5-t-butylacetanilide with copper powder.



(12)

The u.v. spectrum of the second phenazine (6) was similar to that of the first. In addition, a well defined quartet (*J* 10 Hz) in its n.m.r. spectrum was indicative of two *ortho*-coupled protons, and the methoxy-groups now appeared as separate signals. The formation of this material during the oxidation of 5-methoxy-2-(3-methoxy-4-t-butylanilino)-4-t-butylaniline (26) (see later) also constitutes its independent synthesis.

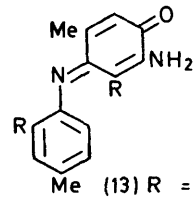
Insufficient quantities of the third phenazine (7), isolated as a gum, prevented its certain identification, but the presence of the phenazine nucleus was revealed by the u.v. spectrum, which was similar to those of (5) and (6). Also, a comparison of the i.r. spectra of the three phenazines provided evidence for the position of the substituents. Thus, the respective absorptions at 885 and 889 cm^{-1} in the spectra of the first two are absent in that of the third, and appear to arise from out-of-plane deformation modes of the isolated ring hydrogen atoms.[14] A band at 779 cm^{-1} in the spectrum of (6) correlates with a strong band at 809 cm^{-1} in the spectrum of (7): these are characteristic of 1,2-disubstituted phenazines.[14] Their absence in the spectrum of (5) and the absence of the out-of-plane deformation bands in that of (7) therefore indicate the substitution pattern of (7). However, bands at 838 and 825 cm^{-1} in the spectra of (5) and (6) cannot be assigned, and this reduces the reliability of these correlations.

The aminoquinone imine (8) was isolated only as a gum, but as it possesses similar spectroscopic properties to the less stable, though crystalline, isomer (9), the identification of their structures is discussed concurrently. The dimeric nature of (8) and (9) was evident from their closely similar n.m.r. spectra, which include signals from two *para* vinylic protons, one methoxy-group, and two t-butyl groups. The amino-quinonoid system was evident from their i.r. spectra (Table). The possibility that one of the bands in the carbonyl region is due to an in-plane bending mode of the primary amino-substituent is made less likely by its persistence in the spectrum of the anilinoquinone imine (21).

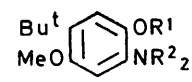
I.r. absorption spectra of quinonoid products in carbon tetrachloride

Compound	$\nu_{max.}/cm^{-1}$	
(8)	3499, 3386	1656, 1626s
(9)	3051m, 3376m	1641m, 1621s
(10)	3505m, 3384m	1636m
(20)	3503m, 3385m	1665s, 1627s
(21)	3348m	1646s, 1627s
(22)	3321m	1632s, 1612s
(23)	3351m	1664s, 1630s

Frémy's salt oxidation of *p*-toluidine [15] and of 1,2,4-xylidine [15,16] gives as sole products the aminoquinone imines (13) and (14), respectively, which have u.v. spectra similar to those of (8) and (9). As reductive



(13) R = H
(14) R = Me



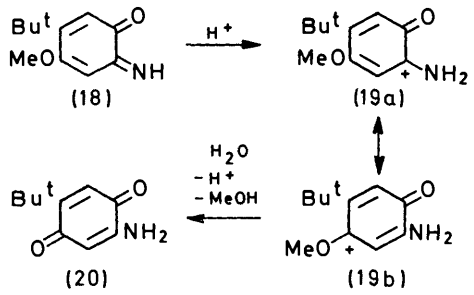
(15) R^1 = Me, R^2 = O
(16) R^1 = H, R^2 = O
(17) R^1 = H, R^2 = H

acetylation of (8) failed to give a crystalline product, its structure was confirmed by synthesis. The dimethoxynitrobenzene (15) was hydrolysed by base in boiling diethyleneglycol dimethyl ether to the nitrophenol (16), which was then reduced to the aminophenol (17). Oxidation of this with silver oxide gave a yellow gum which darkened when exposed to light. Its identity as the quinone imine (18) was established by reductive acetylation to a diacetamide identical with that prepared from the parent aminophenol (17). Attempted purification by chromatography gave a small amount of the *p*-benzoquinone (20), a result consistent with 1,4-addition of water to the protonated quinone imine, followed by loss of methanol (Scheme 1).

When the oxidation was conducted in the presence of the aniline (1) no condensation occurred. However, addition of acetic acid to a mixture of the quinone imine (18) and the aniline (1) caused an immediate reaction; several coloured materials were formed, including the

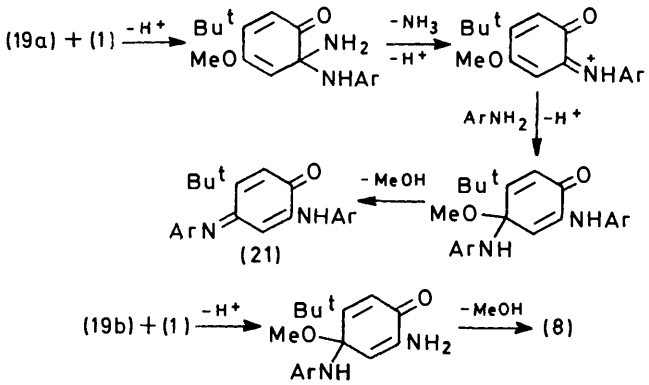
[10] Y. Nomura, H. Anzai, R. Tarao, and K. Shiomi, *Bull. Chem. Soc. Japan*, 1964, **37**, 967.
[11] P. H. Gore and O. H. Wheeler, *J. Org. Chem.*, 1961, **26**, 3295.
[12] G. M. Badger, R. S. Pearce, and R. Petit, *J. Chem. Soc.*, 1951, 3199.
[13] F. R. Hewgill, D. G. Hewitt, and P. B. Langley, *Austral. J. Chem.*, 1965, **18**, 1241.
[14] C. Stammer and A. Taurino, *Spectrochim. Acta*, 1963, **19**, 1625; J. F. Corbett, *ibid.*, 1964, **20**, 1665.
[15] H.-J. Teuber and G. Jellinek, *Chem. Ber.*, 1954, **87**, 1841.
[16] L. Horner and K. Sturm, *Chem. Ber.*, 1955, **88**, 329.

desired aminoquinone imine (8) in 15% yield. The major product was the anilinoquinone imine (21) (61%), whose identity followed from its i.r. spectrum in which secondary amino- and quinonoid bands were evident, and its n.m.r. spectrum which, with signals due to two



SCHEME 1

methoxy- and three t-butyl groups, showed its trimeric nature. The aminoquinone imine (8) was only slowly converted into this material by reaction with the aniline (1) in acetic acid, and this indicates that (8) is not an intermediate in the formation of the anilinoquinone imine (21) during the reaction of (18) with (1). Also, the the use of an excess of the quinone imine (18) in the condensation with (1) did not alter the proportion of the products (8) and (21). We therefore suggest that these products are formed as in Scheme 2, by reaction of either mesomeric form (19a) or (19b) of the protonated quinone imine with the aniline (1).

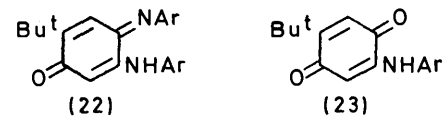


Ar = 3-OMe–4-Bu^{t}C$_6$H$_3$

SCHEME 2

Nevertheless, this synthesis of the aminoquinone imine (8) cannot be regarded as unambiguous, for the generation of the amino-quinone (20) from the quinone imine (18) (Scheme 1) prior to reaction with the aniline (1) is possible, although unlikely. Condensation of the quinone (20) with the aniline (1) could then have given the isomeric quinone imine (9) and the anilinoquinone imine (22). Consequently the quinone (20) was synthesised. The most convenient method proved to be by nitration of t-butylhydroquinone dibenzyl ether, followed by hydrogenolysis of the resulting nitro-compound. The 2-amino-5-t-butylhydroquinone so produced was oxidised in the form of its hydrochloride by silver oxide to the quinone (20). Acid-catalysed condensation of this quinone with the aniline (1) to constitute a direct synthesis of the aminoquinone imine (9) requires initial nucleophilic addition of the aniline to the carbonyl group adjacent to the amine function. Condensation at the alternative carbonyl group would be hindered by the t-butyl group. In hot acetic acid the quinone (20) reacted slowly with the aniline (1) to give the aminoquinone imine (9) (10%). Thus the ambiguity in the synthesis of (8) is removed, and the structures (8) and (9) are established.

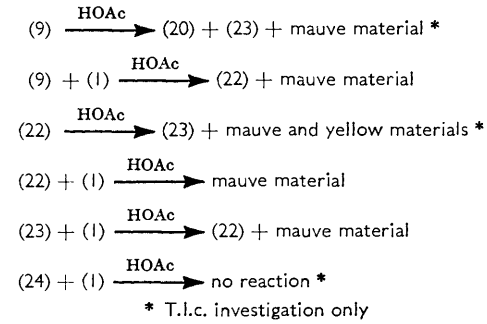
Two other products were isolated from the condensation of (1) with (20), these being the anilino-*N*-arylquinone imine (22) (9·5%) and the anilino-quinone (23) (14%). The n.m.r. spectrum of (22), with signals



Ar = 3-OMe–4-Bu^{t}C$_6$H$_3$

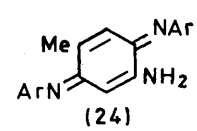
from three t-butyl groups, two methoxy-groups, and two vinylic protons, is in accord with the proposed structure, as is its i.r. spectrum (Table). It may be noted that where a t-butyl group is *ortho* to a carbonyl group, the frequency of the latter is lowered. The structure of the anilinoquinone (23) is assigned on the basis of its n.m.r. spectrum, in which a multiplet characteristic of the anilino-ring protons, and signals from two vinylic protons are evident.

The interrelationship of the products was established by the condensation and hydrolysis reactions shown in Scheme 3. In each case a mauve material which could not be adequately purified appeared among the products.



SCHEME 3

The third quinonoid oxidation product (10) was obtained in very low yield, and like (8) could not be

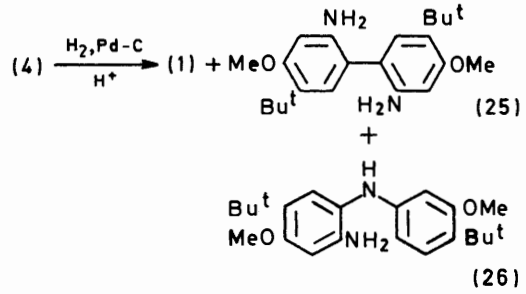


Ar = 4-MeC$_6$H$_4$

crystallised. The amino-group and quinonoid system were evident from its i.r. spectrum (Table), and the

n.m.r. spectrum was consistent with the proposed structure, showing two vinylic protons, and correct integral ratios for the single resonances of two methoxy- and three t-butyl groups. The u.v. spectrum was similar to that of (9). The similarity of compound (10) to Barsilowsky's base (24) suggested that it could be synthesised in the same way.[17] For this purpose the 2-anilinoaniline (26) was required.

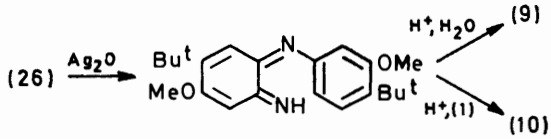
An attempt to prepare this diamine by the *o*-semidine rearrangement of the hydrazobenzene derived from (4) was considered worthwhile, as 4-t-butyl-2-(4-t-butylanilino)aniline is produced in 47% yield by the similar rearrangement of 4,4′-di-t-butylhydrazobenzene.[18] However, hydrogenation of (4) in acid solution gave only traces of the desired diamine (26), the major rearrangement product (as shown in Scheme 4) being the *o*-benzidine (25), identified by its n.m.r. spectrum.



SCHEME 4

The diamine (26) was subsequently prepared by the following route. t-Butylation of *p*-anisidine gave 4-methoxy-3-t-butylaniline, for which proof of the substitution pattern was supplied by an independent preparation from 2-t-butylanisole. Conversion into 4-methoxy-3-t-butylacetanilide followed by nitration gave 4-methoxy-2-nitro-5-t-butylacetanilide, which was hydrolysed to the amine and thence converted into 1-iodo-4-methoxy-2-nitro-5-t-butylbenzene. This was condensed with 3-methoxy-4-t-butylacetanilide, giving the *N*-acetyl-nitro-amine, which was hydrolysed and reduced to the diamine (26).

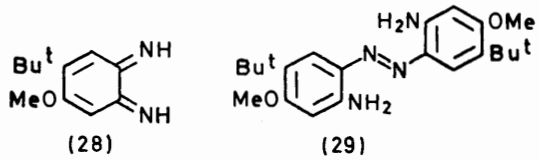
Oxidation of this diamine (Scheme 5) gave a maroon



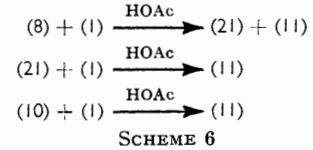
SCHEME 5

material, believed to be the di-imine (27), as well as traces of the phenazines (5) and (6). Although a sample was purified by preparative t.l.c. it could not be crystallised before it decomposed. Hydrogenation gave the parent diamine (26). During column chromatography the di-imine (27) was almost completely hydrolysed to the amino-quinone imine (9), which is in accord with the proposed structure. When a mixture of the di-imine (27) and the aniline (1) was acidified, the major product was compound (10), whose structure is thus confirmed. No condensation took place in neutral solution.

An attempt to prepare the di-imine (28) as an intermediate for the preparation of (27) did not succeed. Oxidation of 4-methoxy-5-t-butyl-*o*-phenylenediamine with silver oxide gave the diaminoazobenzene (29) in 51% yield. Reduction and subsequent acetylation to 4,5-diacetamido-2-t-butylanisole, and deamination to 4,4′-dimethoxy-3,3′-di-t-butylazobenzene established the structure. A small quantity (6%) of the phenazine (5) was also formed in the oxidation. The use of Frémy's salt as an oxidant gave similar results, which suggests that the di-imine (28) may be formed, but rapidly decomposes to the observed products.



The deep blue compound (11), the final oxidation product, was shown to be a tetrameric condensation product by its n.m.r. spectrum, which contained four t-butyl and three methoxy-resonances. Secondary amino- and carbonyl bands were significantly absent in the i.r. spectrum, and the u.v. spectrum, like that of (10), was typical of a *p*-benzoquinone di-imine,[19] rather than of a phenazine. The compound showed marked resistance to hydrolysis by hot acetic acid. The suggested structure (11) is supported by the condensations shown in Scheme 6.

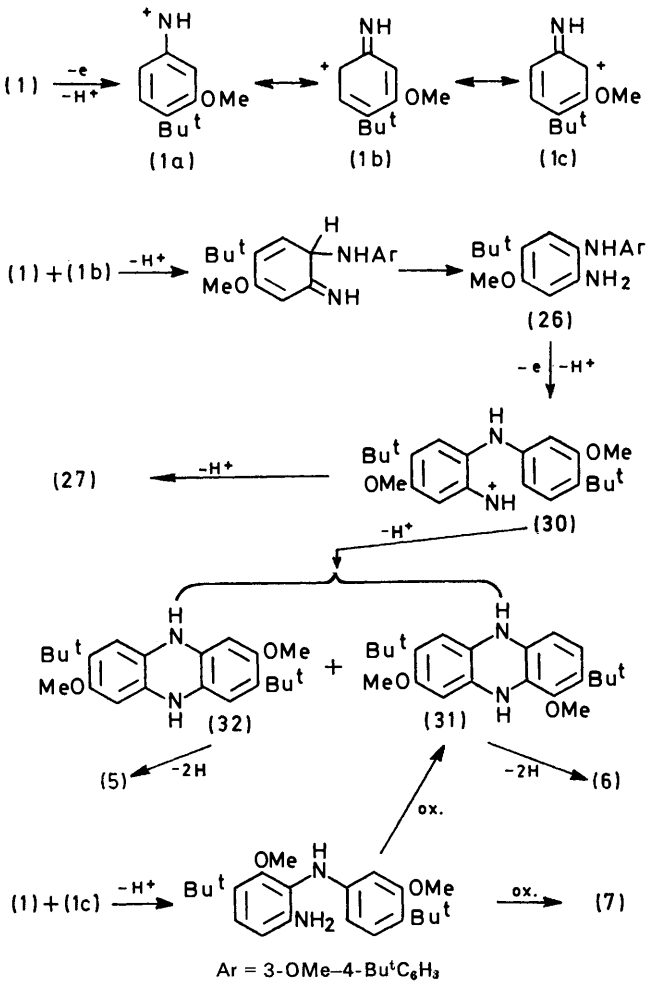


SCHEME 6

Discussion.—The formation of large amounts of the azobenzene (4) appears to be typical of the oxidation of anilines. Although characteristic of the oxidation of naphthylamines,[20-22] phenazines are not usual products from the oxidation of anilines unless alkoxy-[23] or halogeno-[20,24] substituents are present. Morgan and Aubert[25] have suggested a free-radical mechanism for the oxidation of anthranilic acid to phenazine-1,6-di-

[17] A. G. Green, *J. Chem. Soc.*, 1893, 1395; *Ber.*, 1893, **26**, 2772.
[18] H. J. Shine and J. T. Chamness, *J. Org. Chem.*, 1967, **32**, 901.
[19] V. R. Holland, B. M. Roberts, and B. C. Saunders, *Tetrahedron*, 1969, **25**, 2291.
[20] A. G. Hudson, A. E. Pedler, and J. C. Tatlow, *Tetrahedron Letters*, 1968, 2143.
[21] L. Horner and J. Dehnert, *Chem. Ber.*, 1963, **96**, 786.
[22] T. Kawabata, S. Tanimoto, and R. Oda, *Kogyo Kagaku Zasshi*, 1964, **67**, 1151 (*Chem. Abs.*, 1964, **61**, 14,597f).
[23] F. N. Mazitova and R. R. Shagidullin, *Izvest. Akad. Nauk S.S.S.R. Ser. khim.*, 1966, 1851 (*Chem. Abs.*, 1967, **66**, 75,774b); F. N. Mazitova, R. R. Shagidullin, and V. V. Abushaeva, *Zhur. org. Khim.*, 1967, **3**, 878 (*Chem. Abs.*, 1967, **67**, 43,137a).
[24] J. M. Birchall, R. N. Haszeldine, and J. E. G. Kemp, *J. Chem. Soc.* (*C*), 1970, 449.
[25] L. R. Morgan and C. C. Aubert, *Proc. Chem. Soc.*, 1962, 73.

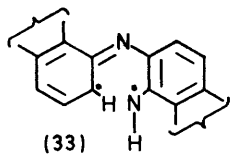
carboxylic acid, and a similar mechanism has been proposed by Horner and Dehnert [21] for the autoxidation of naphthylamines, but having no evidence for or against



SCHEME 7

the involvement of radicals we suggest that the phenazines formed in the oxidation of (1) could also be produced by the cationic route shown in Scheme 7.

In this, the unprotonated form of (30) is the *N*-aryl-*o*-quinone di-imine (27), which can be regarded as a mesomeric form of a diradical analogous to the previously postulated intermediate (33).[21,25] Having pre-



pared compound (27), we thought it of interest to see whether this might in fact be intermediate in phenazine formation. A cyclisation of this kind finds analogy in the Claisen rearrangement, and in the thermal indolisation of phenylhydrazones.[26,27] It is noteworthy that in the silver oxide oxidation of (1) large amounts of maroon material, believed to be (27) were formed, but could not be isolated during the chromatographic separation of the other products. When the di-imine (27) was heated in nitrobenzene at 90° a marked colour change occurred, and the phenazines (5) and (6) were isolated in combined yield of 57—88%. In contrast, when the diamine (26) was so treated the yield of phenazines was lower (37%). On the other hand prolonged silver oxide oxidation of the diamine (26) at room temperature gave yields of phenazines which were no higher than those obtained in the silver oxide oxidation of the aniline (1). It thus appears that the di-imine (27) does not cyclise at room temperature, but is instead hydrolysed to (9) during isolation, and that the precursor of the phenazines is either the ion (30) or a diradical.

Accordingly, the di-imine (27) was warmed in dilute acetic acid in the hope of effecting cyclisation *via* (30), but in this medium large amounts of an unidentified orange material were formed, together with a trace of the quinone imine (9). Treatment with iron(III) chloride also failed to effect cyclisation. Evidence for the participation of (30) has therefore not so far been obtained.

The behaviour of the di-imine (27) and of the diamine (26) on prolonged contact with neutral alumina is also worth noting. After 24 h the former apparently disproportionated to the diamine (26) and the phenazine (5); the amino-quinone imine (9) and other highly coloured products were also formed. The behaviour of the synthetic di-imine and the material isolated from the silver oxide oxidation of (1) was identical in this respect. Under the same conditions the diamine (26) underwent aerial oxidation to the phenazine (5) and an orange material.

Taken together, these observations establish the diamine (26) as the precursor of the phenazines (5) and (6) and of the amino-quinone imine (9), although the exact mechanism of phenazine formation has not been demonstrated.

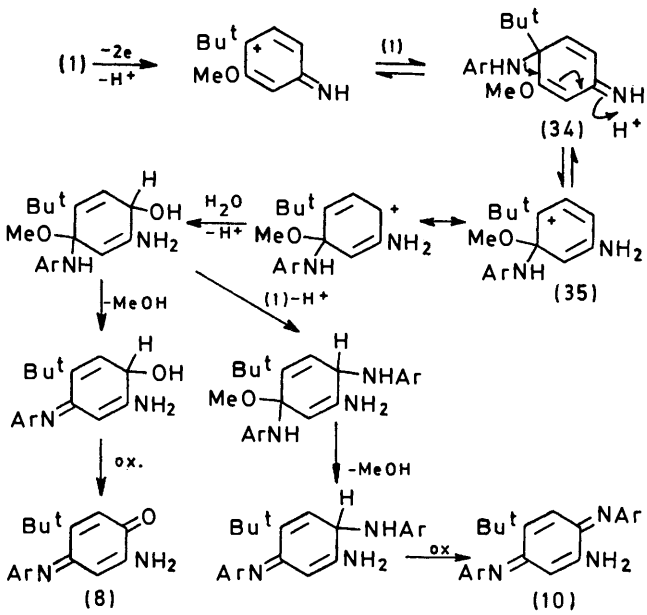
The origin of the quinone imine oxidation products (8) and (10) is less obvious. As they were not produced during oxidation with silver oxide, and could not be detected in the ferricyanide oxidation before chromatography, their formation is presumed to involve more reactive intermediates, either rearranging, or condensing with unchanged (1) on alumina. Various possibilities can be eliminated. Thus (8) does not arise by hydrolysis of (10) on alumina, as (10) is unaffected during chromatography. Consideration of the method of synthesis of (8) (Scheme 2) suggested that the *o*-quinone imine (18) may have been its precursor. Although (18) undergoes acid-catalysed condensation with (1) to give (21) and (8), the latter could well have been the only product of reaction on alumina. However, no such reaction occurred under these conditions.

Contrary to expectations, the quinone imine (10) is not formed by condensation of (8) and (1), as repeated

[26] H. J. Shine, ' Aromatic Rearrangements,' Elsevier, Amsterdam, 1967, p. 205.
[27] B. Robinson, *Chem. Rev.*, 1969, **69**, 227.

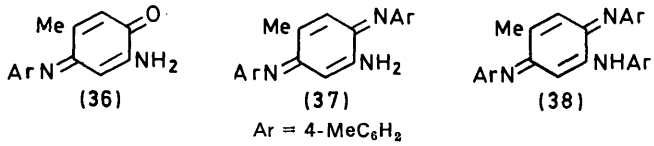
cycling of these compounds through alumina induced no reaction. Moreover, acid-catalysed condensation of (8) with (1) gives (21). A second possibility, the condensation of (1) with the di-imine (27) has already been shown to give (10) under acid conditions (Scheme 5), but the reaction does not occur on alumina, for when a mixture of (1) with (27) was cycled through alumina the product was the blue compound (11), and no trace of (10) was detected. It should be noted that condensation of (10) with (1) to give (11) does not occur on alumina, but requires a more acidic catalyst (Scheme 6). A third possibility, the condensation of quinone imine (9) with (1) was also considered, but again no reaction took place on alumina.

The more obvious routes to the quinone imines (8) and (10) having thus been rejected, it occurred to us that the origin of both compounds could be explained by postulating a *para* carbon–nitrogen coupling of (1) to give the imine (34). The ability of the imino-group to induce 1,4-additions has already been demonstrated, and, on alumina an intramolecular migration of the anilino-portion of (34) to the adjacent reactive position may then be possible. The irreversible elimination of methanol [either before or after hydration or addition of unchanged (1)] from the resultant carbonium ion (35) would then lead directly to the readily oxidised dihydro-precursors of both the quinone imines (8) and (10) (Scheme 8).



SCHEME 8

Although no evidence for Scheme 8 is presented here, some evidence for a similar reaction is presented in the following paper. The envisaged coupling has a sound analogy in phenol oxidation and the proposed rearrangement of (34) is of the dienone–phenol type. Moreover, the reactions of Scheme 8, when applied to the peroxidase oxidation of *p*-toluidine,[28,29] can provide a consistent explanation for the formation of compounds (36)—(38), which are closely related to the quinonoid products (8), (10), and (11) obtained from 3-methoxy-4-t-butylaniline (1), compound (11) being the cyclised analogue of (38).



Even though a scheme involving the iminocyclohexadiene (34) can be written for the formation of the blue compound (11), we consider it more likely that the latter is formed from the di-imine (27), for, as mentioned earlier, this reaction has been shown to take place on alumina.

EXPERIMENTAL

Unless otherwise stated, i.r., u.v., and 60 MHz n.m.r. spectra were measured for solutions in carbon tetrachloride, cyclohexane, and deuteriochloroform, respectively. T.l.c. was carried out on 0·25 mm layers of Ajax silica gel ' S ' activated at 130° for 2 h, or Woelm neutral alumina (pH 7·5) activated at 130° for 3 h. Woelm neutral alumina was generally used for column chromatography, unless ' Activity I ' or ' Activity III ' is specified. The former refers to ' Unilab-LR ' alumina; the latter refers to that prepared by the method of Djerassi *et al.*[30] Silicic acid was the Mallinckrodt 100 mesh product. Ether was dried and distilled from potassium hydroxide before use. Light petroleum had b.p. 56—60°. Anhydrous sodium sulphate was used for drying extracts.

Statement of identity implies no depression of m.p. on admixture (if crystalline), identity of i.r. and n.m.r. spectra, and identity of R_F value and colour on alumina and silica gel in visible and in u.v. light.

3-Methoxy-4-t-butylaniline (1).—(a) *From* N-*acetyl*-m-*anisidine*. t-Butyl chloride (10·0 g), *N*-acetyl-*m*-anisidine (14·9 g) and zinc chloride (20 g) were heated in refluxing carbon disulphide for 60 h. The solution was evaporated and the residue was triturated with water until no zinc chloride remained. The residual material was dissolved in ether and combined with ether extracts of the aqueous washings. Evaporation of the washed and dried ether solution left a gum (18·6 g), which crystallised from ether to give prisms, m.p. 126—127°, of *3-methoxy-4-t-butylacetanilide* (2) (11·8 g, 80%) (Found: C, 70·25; H, 8·7; N, 6·5. $C_{13}H_{19}NO_2$ requires C, 70·55; H, 8·65; N, 6·3%), $\nu_{max.}$ 3446m and 1691s cm^{-1}, τ 1·62 (NH), 2·70 (d, *J* 1·8 Hz, ArH), 2·84 (d, *J* 8·1 Hz, ArH), 3·04 (d × d, *J* 8·1 and 1·8 Hz, ArH), 6·29 (OMe), 7·77 (COMe), and 8·66 (But^t). From the mother liquors *5-methoxy-2,4-di-t-butylacetanilide* (3) (4·5 g) was recovered as long needles, m.p. 218—220° (Found: C, 73·3; H, 10·0; N, 4·9. $C_{17}H_{27}NO_2$ requires C, 73·6; H, 9·8; N, 5·05%), $\nu_{max.}$ 3472m, 3381w, and 1698s cm^{-1}, τ 2·62 (NH), 2·74 and 2·97 (2 × ArH), 6·24 (OMe), 7·83 (*endo*-COMe), 8·08 (*exo*-COMe), and 8·62 (2 × But^t).

Hydrolysis of 3-methoxy-4-t-butylacetanilide (2) (9·2 g) with potassium hydroxide (5 g) in refluxing ethanol (140

[28] B. C. Saunders and P. J. G. Mann, *J. Chem. Soc.*, 1940, 769.
[29] V. R. Holland and B. C. Saunders, *Tetrahedron*, 1966, **22**, 3345.
[30] C. Djerassi, C. H. Robinson, and D. B. Thomas, *J. Amer. Chem. Soc.*, 1956, **78**, 5685.

ml) and water (10 ml) during 60 h gave a brown syrup from which 3-*methoxy*-4-*t*-*butylaniline* (1) (6·0 g, 81%) was obtained by distillation at 95—97° and 0·05 mmHg (Found: C, 73·4; H, 9·4; N, 7·9. $C_{11}H_{17}NO$ requires C, 73·7; H, 9·6; N, 7·8%), $\nu_{max.}$ 3474 and 3391m cm^{-1}, τ 2·93—3·92 (m, 3 × ArH), 6·26 (OMe), 6·59 (NH_2), and 8·68 (Bu^t).

(b) *From* 3-*methoxy*-4-*t*-*butyltoluene*. 3-Methoxy-4-t-butylbenzoic acid, m.p. 151—152° (lit.,[31] 151—152°) was obtained in 72% yield by the oxidation of 3-methoxy-4-t-butyltoluene with potassium permanganate (method of ref. 32 but adding the oxidant over 7 h and heating for a further 4 h). Treatment of the acid with thionyl chloride gave a quantitative yield of 3-*methoxy*-4-*t*-*butylbenzoyl chloride* as pale yellow needles, m.p. 34° (from n-pentane) (Found: C, 63·6; H, 6·6. $C_{12}H_{15}ClO_2$ requires C, 63·6; H, 6·6%). A solution of sodium azide (0·44 g) in water (2 ml) was added dropwise to a stirred solution of the acid chloride (1·08 g) in acetone (5 ml) at 0°. Stirring was continued for 15 min after the initial precipitate had dissolved and the solution had separated into two phases. The mixture was then poured into ice–water (40 ml) and the resultant granular precipitate was dried *in vacuo*. This crude azide (0·98 g) had m.p. 29°. Without further purification it was heated in refluxing sodium-dried benzene (40 ml) for 18 h. Aqueous potassium hydroxide (50%; 3 ml) was then added with vigorous stirring to the cooled solution. The benzene was then distilled off, and the residual alkaline solution was heated on a steam-bath for 15 min, then diluted with water (30 ml) and extracted with light petroleum. Distillation gave the aniline (1) (0·77 g, 90% from the acid chloride) identical with the product from (a). The acetates were also identical.

When the intermediate acid azide (0·49 g) was heated in a smaller volume of refluxing benzene (15 ml) for 4 h, subsequent basification produced both the aniline and *ca.* 30% of *bis*-(3-*methoxy*-4-*t*-*butylphenyl*)*urea*, needles, m.p. 280—283° (from ethanol) (Found: C, 71·7; H, 8·1; N, 7·6. $C_{23}H_{32}N_2O_3$ requires C, 71·8; H, 8·4; N, 7·3%), τ (Me_2SO) 2·78 (d, *J* 2·7 Hz, 2 × ArH), 2·98 (d, *J* 8·8 Hz, 2 × ArH), 3·20 (d × d, *J* 8·8 and 2·7 Hz, 2 × ArH), 6·21 (2 × OMe), and 8·62 (2 × Bu^t), $\nu_{max.}$ (Nujol) 1653s cm^{-1}. Partial hydrolysis to the aniline (1) was achieved by refluxing in aqueous ethanolic potassium hydroxide.

Oxidation of 3-*Methoxy*-4-*t*-*butylaniline* (1).—(a) *By potassium ferricyanide*. 3-Methoxy-4-t-butylaniline (1) (5·37 g) in light petroleum (500 ml) was added dropwise under nitrogen during 5 h to a stirred solution of potassium ferricyanide (21·7 g, 2·2 equiv.) and sodium hydroxide (1·4 g) in deoxygenated water (600 ml) at room temperature. After a further 12 h stirring the deep red organic layer was separated, washed with water, dried, and evaporated under reduced pressure to yield a dark crystalline residue. Extraction with light petroleum left an orange material (953 mg), which was recrystallised from chloroform to give 3,3′-*dimethoxy*-4,4′-*di*-*t*-*butylazobenzene* (4) as orange prisms, m.p. 212—213° (Found: C, 74·0; H, 8·4; N, 7·95. $C_{22}H_{30}N_2O_2$ requires C, 74·5; H, 8·5; N, 7·9%), $\lambda_{max.}$ ($CHCl_3$) 252, 365, and 440sh nm (log ε 3·98, 4·04, and 3·24), τ 2·6 (s, 6 × ArH), 6·08 (2 × OMe), and 8·58 (2 × Bu^t).

The light petroleum extracts were chromatographed on alumina to give six major fractions.

Fraction 1, eluted by light petroleum, comprised the azobenzene (4) (630 mg) and a brown-red band, which was subjected to preparative t.l.c. on silica gel in benzene to give an orange-brown gum (12 mg) of 2-*amino*-NN′-*bis*-(3-*methoxy*-4-*t*-*butylphenyl*)-5-*t*-*butylcyclohexa*-2,5-*diene*-1,4-*diimine* (10), $\nu_{max.}$ 3505m, 3384m, and 1636m cm^{-1}, $\lambda_{max.}$ 225, 307, and 446 nm (log ε *ca.* 4·1, 4·1, and 3·7), τ (CCl_4) 2·70—3·92 (m, 6 × ArH), 3·27 and 4·26 (2 vinylic H), 5·49 (NH_2), 6·16 (2 × OMe), and 8·60 (3 × Bu^t).

Fraction 2, eluted by light petroleum–ether (19 : 1) was a dark red gum and was rechromatographed on Activity I alumina to give four main fractions, (i)—(iv). The first (i), eluted by light petroleum, deposited crystals of the azobenzene (4) (21 mg). The mother liquors were combined with fraction (ii), eluted by light petroleum–ether (19 : 1 to 9 : 1), which was then applied to silicic acid. Light petroleum eluted small quantities of the azobenzene (4) and light petroleum–ether (9 : 1) a pale yellow gum, which deposited yellow needles, m.p. 159—161°, of 1,8-*dimethoxy*-2,7-*di*-*t*-*butylphenazine* (6) (13 mg) (Found: C, 75·2; H, 8·3; N, 7·9. $C_{22}H_{28}N_2O_2$ requires C, 75·0; H, 8·0; N, 7·95%), $\lambda_{max.}$ 218, 267, 367sh, and 382 nm (log ε 4·19, 4·68, 3·78, and 3·95), τ (CCl_4) 2·01 (ArH), 2·21 and 2·30 (q, *J* 10·0 Hz, 2 × ArH), 2·63 (ArH), 5·65 and 5·93 (2 × OMe), and 8·46 (2 × Bu^t). Under u.v. light (6) exhibited a yellow fluorescence on silica gel and an orange green fluorescence on alumina. The n-pentane mother liquors from the crystallisation of (6) were chromatographed on activated silicic acid to give traces of a yellow gum believed to be 1,6-*dimethoxy*-2,7-*di*-*t*-*butylphenazine* (7), $\lambda_{max.}$ 206, 272, 355sh, and 374 nm. Under u.v. light the fluorescence on both silica gel and alumina was orange.

Fraction (iii), eluted by light petroleum–ether (9 : 1 to 4 : 1), was a light brown gum which was rechromatographed on activated silicic acid to give a small quantity of the phenazine (6) and 3,8-*dimethoxy*-2,7-*di*-*t*-*butylphenazine* (5) (62 mg), pale yellow needles, m.p. 204—205° (from light petroleum) (Found: C, 75·0; H, 7·9; N, 8·0. $C_{22}H_{28}N_2O_2$ requires C, 75·0; H, 8·0; N, 7·95%), $\lambda_{max.}$ 228, 265, 348sh, and 358 nm (log ε 4·05, 4·70, 3·44, and 3·60), τ (CCl_4) 2·04 (2 × ArH), 2·56 (2 × ArH), 5·88 (2 × OMe), and 8·45 (2 × Bu^t). This phenazine exhibited a pale yellow-green fluorescence on silica gel, and a striking, bright green fluorescence on alumina in u.v. light.

Fraction (iv), eluted by light petroleum–ether (4 : 1 to 11 : 9), was red and was rechromatographed on activated silicic acid. Light petroleum eluted a red band which was rechromatographed to give 2-*amino*-4-(3-*methoxy*-4-*t*-*butylphenylimino*)-5-*t*-*butylcyclohexa*-2,5-*dien*-1-*one* (8) (110 mg) as a dark maroon-red gum, $\nu_{max.}$ 3499m, 3386m, 1656m, and 1626s cm^{-1}, $\lambda_{max.}$ 217 and 237sh, and 287 nm (log ε *ca.* 4·35, 4·2, and 4·1), τ (CCl_4) 2·86 (d, *J* 8·0 Hz, ArH), 3·73 and 3·88 (s + d × d, *J* 8·0 and 2·0 Hz, 2 × ArH), 3·54 and 4·16 (2 vinylic H), 5·67 (NH_2), 6·18 (OMe), 8·55, and 8·63 (2 × Bu^t). This material could not be crystallised.

Fraction 3, eluted by light petroleum–ether (9 : 1 to 4 : 1) consisted largely of 3-methoxy-4-t-butylaniline (1) (1·63 g) and dark brown material. The aniline was recovered by extraction with sulphuric acid.

Fraction 4, eluted by light petroleum–ether (4 : 1) consisted of more of the unchanged aniline (1) and deep blue, green, and brown materials. The blue component was separated by its strong adsorption on silicic acid, then rechromatographed on alumina to give 10,N-*bis*-(3-*methoxy*-4-*t*-*butylphenyl*)-7-*methoxy*-3,8-*di*-*t*-*butyl*-10H-*phenazin*-2-*imine* (11) (80 mg) as deep blue needles, m.p. 202—204° (from

[31] D. S. Noyce and L. J. Dolby, *J. Org. Chem.*, 1961, **26**, 1732.
[32] W. van Hartingsveldt, P. E. Verkade, and B. M. Wepster, *Rec. Trav. chim.*, 1956, **73**, 349.

light petroleum) (Found: C, 78·1; H, 8·5; N, 6·2%; *M* (mass spec.), 661. $C_{43}H_{55}N_3O_3$ requires C, 78·0; H, 8·4; N, 6·35%; *M*. 661), $\lambda_{max.}$ 235, 317, and 575 nm (log ε 3·74, 3·67, and 4·12), $\nu_{max.}$ 1616w cm^{-1}, τ 2·42—3·78 (*ca.* 9H, m), 4·42 (vinylic H), 6·02, 6·22, and 6·25 (3 × OMe), and 8·37, 8·59, 8·67, and 8·73 (4 × Bu^t).

Fraction 5, eluted by light petroleum–ether (2·5 : 1 to 1 : 1), was taken up in ether and washed with ice-cold sulphuric acid to remove unchanged (1). After extensive washing and drying the ether was removed under reduced pressure at room temperature. Rechromatography of the residue on alumina gave *5-amino-4-(3-methoxy-4-t-butylphenylimino)-2-t-butylcyclohexa-2,5-dien-1-one* (9) (60 mg) as fine orange blades, m.p. 165—166·5° (from ether–light petroleum) (Found: C, 74·1; H, 8·6; N, 8·3. $C_{21}H_{26}N_2O_2$ requires C, 74·1; H, 8·3; N, 8·2%), $\nu_{max.}$ 3501m, 3376m, 1641m, and 1621s cm^{-1}, $\lambda_{max.}$ 218, 286, and 430 nm (log ε 4·38, 4·30, and 3·79), τ (CCl_4) 2·82 (d, *J* 8·0 Hz, ArH), 3·61 and 3·85 (s + d × d, *J* 8·0 and 2·0 Hz, 2 × ArH), 3·33 and 4·37 (2 vinylic H), 4·50 (NH_2), 6·18 (OMe), 8·62, and 8·80 (2 × Bu^t). A further 22 mg of (9) was recovered by chromatography of preceding and subsequent fractions.

Fraction 6. More polar solvents eluted dark glassy materials which were not further examined.

The use of a five-fold excess of oxidant or reverse addition of the reactants did not significantly change the relative yields of the azobenzene and phenazines, whereas variable yields of the quinonoid products were encountered under these and the foregoing oxidation conditions.

A light petroleum solution of the oxidation products prior to chromatographic separation was shown by t.l.c. on alumina and silica gel to contain the azobenzene and the phenazines, but none of the products (8)—(11) were detected. A maroon material also present had an R_F value similar to that of the *o*-quinone di-imine (27).

(b) *By silver oxide.* A solution of the aniline (1) (5·37 g) was shaken with silver oxide (16 g) in ether (400 ml) at room temperature for 72 h. The red mixture was filtered, and the filtrate was evaporated under reduced pressure at room temperature leaving a red crystalline residue. Extraction of this with light petroleum gave the azobenzene (4) (1·83 g). T.l.c. of the light petroleum extracts indicated the presence of the azobenzene, the three phenazines, an orange material of intermediate R_F value, unchanged aniline (1), and a large amount of maroon material apparently identical with (27). Chromatographic separation of the extracts gave (7) (trace amount), (6) (30 mg), (5) (110 mg), (9) (350 mg), (11) (60 mg), and unchanged (1) (74 mg).

Reductive Acetylation of 3,3'-Dimethoxy-4,4'-di-t-butylazobenzene (4).—The azobenzene (500 mg), zinc dust (500 mg), and sodium acetate (300 mg) were heated in refluxing acetic anhydride (10 ml). When the mixture was colourless (5 min) it was poured into dilute sulphuric acid. Extraction with ether gave 3-methoxy-4-t-butylacetanilide (2) identical with the material already described.

Reductive Acetylation of 3,8-Dimethoxy-2,7-di-t-butylphenazine (5).—The phenazine (5) (50 mg) was heated with zinc dust and sodium acetate in refluxing acetic anhydride for 15 min to give *5,10-diacetyl-3,8-dimethoxy-2,7-di-t-butyl-5,10-dihydrophenazine* (12) (22 mg) as small needles, m.p. 277—279° (from chloroform) (Found: C, 71·3; H, 7·6. $C_{26}H_{34}N_2O_4$ requires C, 71·2; H, 7·8%), $\nu_{max.}$ (CH_2Cl_2) 1661s cm^{-1}, τ 2·72 (2 × ArH), 2·77 (2 × ArH), 6·15 (2 × OMe), 7·62 (2 × COMe), and 8·63 (2 × Bu^t).

4-Methoxy-3-t-butylaniline.—(*a*) *p*-Anisidine (53·5 g) and sulphuric acid (50%; 100 ml) were carefully mixed in an ice–salt bath to reduce the possibility of sulphonation.[33] The cold mixture was then carefully treated with more sulphuric acid (95%; 250 ml). t-Butyl alcohol (37 g) was then added to the stirred solution at room temperature during 12 h. After a further 36 h stirring, more t-butyl alcohol (37 g) was similarly added, and stirring was continued until a total of 96 h had elapsed. Quenching of the resultant purple solution with ice (1 kg) precipitated white crystals which were filtered off and washed with dry ether. The crystals were then treated with aqueous ammonia (30%) and the resultant red oil was taken up in light petroleum. Distillation of the washed and dried extracts gave *4-methoxy-3-t-butylaniline* (53 g, 63%), b.p. 114—116° at 0·2 mmHg, which crystallised from n-pentane as needles, m.p. 36·5—37·5° (Found: C, 73·5; H, 9·5; N, 7·4. $C_{11}H_{17}NO$ requires C, 73·7; H, 9·6; N, 7·8%), τ 3·22—3·62 (m, 3 × ArH), 6·26 (OMe), 6·86 (NH_2), and 8·67 (Bu^t). The acetanilide had m.p. 130—131° (lit.,[34] 126·5—127°).

(*b*) Treatment of 2-t-butylanisole (13·4 g) with nitric acid (90%; 17 ml) by the 'Type C' nitration method of Carpenter, Easter, and Wood,[35] at −10° gave a yellow oil (16·0 g) from which *4-nitro-2-t-butylanisole* (7·0 g, 39%) was obtained as yellow needles, m.p. 62—63° (Found: C, 63·1; H, 7·4. $C_{11}H_{15}NO_3$ requires C, 63·4; H, 7·2%) by crystallisation from aqueous ethanol. Hydrogenation in methanol over palladium–charcoal gave 4-methoxy-3-t-butylaniline (95%).

Synthesis of 3,8-Dimethoxy-2,7-di-t-butylphenazine (5).—Bromine (2·4 g) in chloroform (10 ml) was added dropwise to a stirred ice-cold solution of 4-methoxy-3-t-butylacetanilide (3·3 g) in chloroform (20 ml). The mixture was washed with aqueous sodium hydrogen sulphite, then water, and after removal of the solvent, crystallisation from ether–light petroleum gave *2-bromo-4-methoxy-5-t-butylacetanilide* (4 g, 89%) as prisms, m.p. 161·5—162·5° (Found: C, 52·3; H, 6·0; Br, 26·6. $C_{13}H_{18}BrNO_2$ requires C, 52·0; H, 6·0; Br, 26·65%), τ 2·01 and 3·02 (2 × ArH), 6·21 (OMe), 7·84 (COMe), and 8·67 (Bu^t). Hydrolysis by boiling for 2 h in acetic acid–50% sulphuric acid (2 : 1) gave *2-bromo-4-methoxy-5-t-butylaniline*, which crystallised from ether–light petroleum as plates, m.p. 47—48° (Found: C, 51·0; H, 6·6; Br, 30·9. $C_{11}H_{16}BrNO$ requires C, 51·2; H, 6·3; Br, 30·95%).

2-Bromo-4-methoxy-5-t-butylacetanilide (240 mg), potassium carbonate (240 mg), and copper powder (20 mg) were heated at 200° for 36 h. The resultant dark solid was crushed and extracted with boiling light petroleum. Application of the filtered extracts to Activity I alumina and elution with light petroleum–ether (4 : 1) gave a phenazine (10 mg) identical with (5).

2-Hydroxy-5-methoxy-4-t-butylaniline (17).—2,5-Dimethoxy-4-t-butylnitrobenzene (15) (6·3 g)[8] and potassium hydroxide (10 g) were stirred in refluxing diethylene glycol dimethyl ether (150 ml) for 6 h. The mixture was poured into water and the nitrophenol (16) (2·8 g) was isolated by a standard method.[36] To the phenol (1·1 g) in aqueous sodium hydroxide (5%; 50 ml) at 60—70°, was added sodium

[33] S. I. Burmistrov and G. E. Krakovtseva, *Zhur. obshchei Khim.*, 1962, **32**, 2003 (*Chem. Abs.*, 1963, **58**, 5552f).
[34] S. I. Burmistrov and N. V. Ponomarev, *Zhur. obshchei Khim.*, 1962, **32**, 1515 (*Chem. Abs.*, 1963, **58**, 3338d).
[35] M. S. Carpenter, W. M. Easter, and T. F. Wood, *J. Org. Chem.*, 1951, **16**, 586.
[36] H. E. Ungnade and I. Ortega, *J. Org. Chem.*, 1952, **17**, 1475.

dithionite with stirring until the sodium phenolate had dissolved and the red solution had become colourless. Acidification produced a precipitate which was recrystallised from ether–light petroleum to give 2-*hydroxy*-5-*methoxy*-4-*t*-*butylaniline* (17) (0·88 g, 90%) as fine needles, m.p. 150—150·5° (decomp.) (Found: C, 68·0; H, 8·9; N, 7·1. $C_{11}H_{17}NO_2$ requires C, 67·7; H, 8·8; N, 7·2%). The *diacetate* crystallised from methanol as fine needles, m.p. 163—164° (Found: C, 64·7; H, 7·6. $C_{15}H_{21}NO_4$ requires C, 64·5; H, 7·6%).

6-*Imino*-4-*methoxy*-3-*t*-*butylcyclohexa*-2,4-*dien*-1-*one* (18).—2-Hydroxy-5-methoxy-4-t-butylaniline (17) (100 mg) was shaken with silver oxide (1·0 g) and anhydrous sodium sulphate in ether (75 ml) in the dark for 30 min. The mixture was filtered and the ether was evaporated off in darkness under reduced pressure to leave the o-*quinone imine* (18) (88 mg) as an unstable brownish yellow gum, $\nu_{max.}$ 3201m, 1666s, and 1611s cm^{-1}. Reductive acetylation gave a diacetate (91 mg), identical with that obtained from the parent amino-phenol. Attempted purification of the quinone imine by rapid chromatography on neutral alumina gave dark green and brown materials. The fraction eluted by light petroleum–ether (7 : 3) was shown by comparative t.l.c. to contain 2-amino-5-t-butyl-1,4-benzoquinone (20). No phenazine (5) was detected in any of the fractions.

2-*Amino*-5-*t*-*butyl*-1,4-*benzoquinone* (20).— Potassium hydroxide (10·2 g) in dry ethanol (240 ml) was added dropwise during 6 h to a refluxing solution of t-butylhydroquinone (13·2 g) and benzyl chloride (22·2 g) in ethanol (100 ml) under nitrogen. After a further 12 h heating the solvent was evaporated off under reduced pressure and water (250 ml) was added. Extraction with and crystallisation from ether gave 1,4-*dibenzyloxy*-2-*t*-*butylbenzene* (24·2 g, 88%) as needles, m.p. 98—98·5° (Found: C, 82·9; H, 7·25. $C_{24}H_{26}O_2$ requires C, 83·2; H, 7·6%).

Dropwise addition of nitric acid (35%; 34 ml) to a stirred solution of the dibenzyl ether (12·3 g) in acetic acid (125 ml) at room temperature during 2 h gave a pale yellow precipitate which was crystallised from methanol to give 2,5-*dibenzyloxy*-1-*nitro*-4-*t*-*butylbenzene* (13 g, 94%) as plates, m.p. 160—160·5° (Found: C, 73·5; H, 6·4. $C_{24}H_{25}NO_4$ requires C, 73·6; H, 6·4%).

Heating this product (2·5 g) in acetic acid (60 ml) and concentrated hydrochloric acid (4 ml) on a steam-bath for 30 h partly converted it into 4-*benzyloxy*-2-*nitro*-5-*t*-*butylphenol* (0·6 g), which crystallised from light petroleum as elongated prisms, m.p. 115—116·5° (Found: C, 67·6; H, 6·5. $C_{17}H_{19}NO_4$ requires C, 67·8; H, 6·4%). 2,5-Dibenzyloxy-1-nitro-4-t-butylbenzene (7·8 g) in absolute ethanol saturated with dry hydrogen chloride was shaken with 10% palladium–charcoal under hydrogen. When the rapid hydrogen uptake had ceased, the solution was filtered and evaporated under reduced pressure to leave a pale green crystalline residue (4·3 g), which was not purified but oxidised directly to the quinone (20). Acetylation of a portion of the crude aminophenol hydrochloride gave 2,5-*diacetoxy*-NN-*diacetyl*-4-*t*-*butylaniline*, needles, m.p. 120—121° (from methanol) (Found: C, 61·5; H, 6·7; N, 4·2. $C_{18}H_{23}NO_6$ requires C, 61·9; H, 6·6; N, 4·0%), τ 2·77 and 3·03 (2 × ArH), 7·70 (3 × COMe), 7·80 (COMe), and 8·63 (Bu^t).

The crude aminophenol hydrochloride (217 mg) was shaken for 15 min in ether (80 ml) with silver oxide (1·16 g) and anhydrous sodium sulphate. After filtration the ether was evaporated off under reduced pressure to leave a maroon coloured residue, which after application to alumina and elution with light petroleum–ether (4 : 1) gave 2-*amino*-5-*t*-*butyl*-1,4-*benzoquinone* (20) (180 mg) as elongated red blades, m.p. 111—112° (from ether–light petroleum) (Found: C, 67·15; H, 7·3; N, 7·8. $C_{10}H_{13}NO_2$ requires C, 67·0; H, 7·3; N, 7·8%), $\nu_{max.}$ 3503m, 3385m, 1665s, and 1627s cm^{-1}, τ 3·53 and 4·32 (2 vinylic H), 4·91 (NH_2), and 8·70 (Bu^t). Reductive acetylation gave a tetra-acetate identical with that already described.

Condensations of 3-*Methoxy*-4-*t*-*butylaniline* (1).—(a) *With* 6-*imino*-4-*methoxy*-3-*t*-*butylcyclohexa*-2,4-*dien*-1-*one* (18). A solution in acetic acid (5 ml) of the *o*-quinone imine (18) [from the aminophenol (17) (195 mg)] and the aniline (1) (179 mg) was heated gently on a steam-bath for 5 min. Ether was added to the resultant dark red-purple solution, which after successive washings with water, aqueous sodium hydrogen carbonate, and water was dried and evaporated leaving a dark purple crystalline residue. Extraction of this with light petroleum left 2-(3-*methoxy*-4-*t*-*butylanilino*)-4-(3-*methoxy*-4-*t*-*butylphenylimino*)-5-*t*-*butylcyclohexa*-2,5-*dien*-1-*one* (21) (161 mg) as purple needles, m.p. 185—186° (from ether) (Found: C, 76·5; H, 8·5; N, 5·5. $C_{32}H_{42}N_2O_3$ requires C, 76·5; H, 8·4; N, 5·6%), $\nu_{max.}$ 3348m, 1646s, and 1627s cm^{-1}, τ 2·80—3·93 (8H, m), 6·23 and 6·46 (2 × OMe), and 8·52, 8·62, and 8·70 (3 × Bu^t). The light petroleum extracts were chromatographed on alumina to give a small amount of (21) and a red gum (51 mg) which was identical with compound (8). Small amounts of other highly coloured materials were present, but the phenazine (5) was not detected.

The proportions of the condensation products were not appreciably altered by using an excess of the amino-phenol (17) in the initial oxidation and no reaction could be detected in neutral solution after 12 h by t.l.c. or reductive acetylation.

(b) *With* 2-*amino*-4-(3-*methoxy*-4-*t*-*butylphenylimino*)-5-*t*-*butylcyclohexa*-2,5-*dien*-1-*one* (8). This compound (8) (16 mg) and the aniline (1) in acetic acid gave, after 4 h [processing as described in (a)] a purple gum which deposited crystals of the anilino-quinone imine (21) (8 mg) from light petroleum. Fractionation of the mother liquors on alumina gave a small quantity of the unchanged amino-quinone imine (8) and the blue compound (11).

(c) *With* 2-(3-*methoxy*-4-*t*-*butylanilino*)-4-(3-*methoxy*-4-*t*-*butylphenylimino*)-5-*t*-*butylcyclohexa*-2,5-*dien*-1-*one* (21). An acetic acid solution (8 ml) of the aniline (1) (75 mg) and the anilino-quinone imine (21) (106 mg) was heated on a steam-bath for 8 h. Formation of a blue-grey material of low R_F value became predominant after this time, although unchanged (21) was still present. Treatment of the reaction mixture as in (a) afforded a deep blue residue which was chromatographed on silicic acid to give unchanged (21) (78 mg), a deep blue material, and a mixture of this with 3-methoxy-4-t-butylacetanilide. Chromatography of this mixture on alumina gave the blue compound (11).

(d) *With* 2-*amino*-NN′-*bis*-(3-*methoxy*-4-*t*-*butylphenyl*)-5-*t*-*butylcyclohexa*-2,5-*dien*-1,4-*di*-*imine* (10). Reaction of this compound (10) (3 mg) with excess of aniline (1) in acetic acid gave, after 50 min, a grey gum, from which the blue compound (11) was recovered as a gum (*ca.* 1 mg) by preparative t.l.c. Its i.r. spectra and R_F values were identical with those recorded for (11).

(e) *Attempted condensations with compounds* (18), (8), *and* (10) *on neutral alumina.* The aniline (1) did not condense with any of these three compounds when solutions of the

appropriate mixtures in light petroleum–ether (4 : 1) were cycled through neutral alumina.

(f) *With 2-amino-5-t-butyl-1,4-benzoquinone* (20). Reaction of the aniline (1) (54 mg) with the quinone (20) (54 mg) in acetic acid on a steam-bath gave, after 5 h, a deep red residue which was chromatographed on alumina. Light petroleum–ether (9 : 1) eluted a maroon band, from which was recovered 2-(3-*methoxy*-4-*t*-*butylanilino*)-5-*t*-*butyl*-1,4-*benzoquinone* (23) (16 mg) as brownish purple prisms, m.p. 162·5—164° (from light petroleum) (Found: C, 74·2; H, 8·1; N, 4·3. $C_{21}H_{27}NO_3$ requires C, 73·9; H, 8·0; N, 4·1%), $\nu_{max.}$ 3351m, 1664s, and 1630s cm^{-1}, τ 2·72—3·33 (m, 3 × ArH), 3·46 and 3·98 (2 vinylic H), 6·18 (OMe), and 8·64 and 8·68 (2 × Bu^t).

Repeated rechromatography of the mother liquors on Activity 1 alumina gave a red-brown gum (16 mg) [light petroleum–ether (9 : 1)] which deposited 5-(3-*methoxy*-4-*t*-*butylanilino*)-4-(3-*methoxy*-4-*t*-*butylphenylimino*)-2-*t*-*butylcyclohexa*-2,5-*dien*-1-*one* (22) as brownish red prisms, m.p. 187—189° (from n-pentane) (Found: C, 76·2; H, 8·6; N, 5·6. $C_{32}H_{42}N_2O_3$ requires C, 76·5; H, 8·4; N, 5·6%), $\nu_{max.}$ 3321m, 1623s, and 1612s cm^{-1}, τ 2·17br (NH), 2·55—3·42 (m, 6 × ArH), 3·45 and 3·86 (2 vinylic H), 6·14 (2 × OMe), and 8·57, 8·62, and 8·74 (3 × Bu^t).

Further chromatography of an orange band which was eluted from the original column by light petroleum–ether (7 : 3) gave unchanged (20) (5 mg) and (9) (10 mg).

(g) *With the anilino-quinone* (23), *the amino-quinone imine* (9), *and the anilino-quinone imine* (22). A similar sequence of reactions to those described in (f) gave from (1) (10 mg) and (23) (10 mg) the anilino-quinone imine (22) (8 mg) and mauve gum (7 mg) after reaction for 3 h. From (1) (22 mg) and (9) (41 mg) after reaction for 5 h the same products, (22) (15 mg), and mauve gum (7 mg), were obtained, and from excess of (1) and (22) (15 mg) after 7 h only the mauve gum (10 mg) was obtained. This mauve gum did not react with the aniline (1) under these conditions.

Acidic Hydrolysis of the Blue Compound (11).—In acetic acid (3 ml containing a drop of water) compound (11) slowly decomposed on a steam-bath during 6 h to a blue-grey material apparently identical with the material described in (c).

Acidic Hydrolysis of 5-Amino-4-(3-methoxy-4-t-butylphenylimino)-2-t-butylcyclohexa-2,5-dien-1-one (9).—A solution of (9) (5 mg) in acetic acid was heated on a steam-bath for 7 h. Removal of the acid left a red-brown residue which was shown by t.l.c. to contain the anilino-quinone (23), the aminoquinone (20), and the mauve material.

Acidic Hydrolysis of 5-(3-*Methoxy*-4-*t*-*butylanilino*)-4-(3-*methoxy*-4-*t*-*butylphenylimino*)-2-*t*-*butylcyclohexa*-2,5-*dien*-1-*one* (22).—Similar treatment of this compound (22) (5 mg) gave a deep red gum, which was shown by t.l.c. to contain the anilino-quinone (23), the mauve gum, and a yellow band of low R_F value.

Purification of the Mauve Material.—Fractionation by preparative t.l.c. on neutral alumina in benzene–n-hexane (1 : 1) of the crude material gave only the mauve gum, which could not be crystallised. It had $\nu_{max.}$ 3426br,w, 3171w, 1739m, and 1625s cm^{-1}, τ 2·35—3·34 (*ca.* 7H, m), 4·37 (vinylic H), 6·03 and 6·18 (2 × OMe), 8·53 (2 × Bu^t), and 8·72 (Bu^t).

4-*Methoxy*-5-*t*-*butyl*-o-*phenylenediamine*.—Dropwise addition of nitric acid (70%; 19·7 ml) in acetic acid (50 ml) to a stirred solution of 4-methoxy-3-t-butylacetanilide (22·1 g) in acetic acid (500 ml) at 20° during 2 h produced a yellow precipitate. After addition of water (500 ml) the product was filtered off and recrystallised from methanol to give 4-*methoxy*-2-*nitro*-5-*t*-*butylacetanilide* (23·1 g, 87%) as fine yellow needles, m.p. 194—195° (Found: C, 58·9; H, 7·0; N, 10·4. $C_{13}H_{18}N_2O_4$ requires C, 58·6; H, 6·8; N, 10·5%), τ −0·21 (NH), 1·22 and 2·36 (2 × ArH), 6·09 (OMe), 7·73 (COMe), and 8·59 (Bu^t). Hydrolysis in refluxing absolute methanol containing dry hydrogen chloride for 45 min [37] gave 4-*methoxy*-2-*nitro*-5-*t*-*butylaniline* as red needles, m.p. 176—177° (from methanol), in quantitative yield (Found: C, 59·2; H, 7·3. $C_{11}H_{16}N_2O_3$ requires C, 58·9; H, 7·2%).

Reduction of this amine over palladium–charcoal in methanol gave 4-*methoxy*-5-*t*-*butyl*-o-*phenylenediamine*, b.p. 136—140° at 0·01 mmHg, needles, m.p. 98—99·5° (from light petroleum–ether) (Found: C, 68·2; H, 9·1; N, 14·1. $C_{11}H_{18}NO_2$ requires C, 68·0; H, 9·3; N, 14·4%). Treatment overnight with cold acetic anhydride–acetic acid gave the NN′-*diacetamide*, which crystallised as prisms, m.p. 177—178° (from ether) (Found: C, 64·5; H, 8·0. $C_{15}H_{22}N_2O_3$ requires C, 64·7; H, 8·0%), $\nu_{max.}$ 3243s, 3188s, 3123m, 3049m, and 1660s cm^{-1}, τ 2·94 (ArH), 3·06 (ArH), 6·22 (OMe), 7·97 (2 × COMe), and 8·68 (Bu^t).

Oxidation of 5-*Methoxy*-4-*t*-*butyl*-o-*phenylenediamine*.—(a) *By silver oxide.* A solution of the diamine (194 mg) in ice-cold ether (150 ml) was shaken with silver oxide (1·9 g) and anhydrous sodium sulphate for 40 min. The mixture was filtered and evaporated under reduced pressure to leave a dark crystalline residue. Recrystallisation from ether gave orange-yellow needles (98 mg), m.p. 258—260°, of 2,2′-*diamino*-4,4′-*dimethoxy*-5,5′-*di*-*t*-*butylazobenzene* (29) (Found: C, 68·85; H, 8·3; N, 14·4. $C_{22}H_{32}N_4O_2$ requires C, 68·7; H, 8·4; N, 14·6%), $\lambda_{max.}$ ($CHCl_3$) 249, 277, 322, and 464 nm (log ε 3·95, 4·15, 3·88, and 4·27), τ 2·43 (2 × ArH), 3·81 (2 × ArH), 4·44br (NH_2), 6·15 (2 × OMe), and 8·61 (2 × Bu^t). Chromatography of the mother liquors on alumina gave 3,8-dimethoxy-2,7-di-t-butylphenazine (5) (10 mg), and traces of unidentified coloured materials. No other products were isolated when the oxidation was conducted in the dark, either alone or in the presence of aniline (1) or 2,5-dimethoxy-4-t-butylaniline.

(b) *By Frémy's salt.* The diamine (194 mg) in ether (20 ml) at 0° was added to a solution of Frémy's salt (590 mg) in ice-cold aqueous potassium dihydrogen phosphate (0·1M; 50 ml) and sodium hydroxide (0·1M; 25·9 ml). Immediate reaction occurred, and after shaking for 1 min, the ethereal layer was separated, washed with ice–water, dried, and evaporated to leave an orange gum. Addition of light petroleum gave the diaminoazobenzene (29). T.l.c., which showed the phenazine (5) to be present in the mother liquors, also indicated that no 5-methoxy-4-t-butyl-1,2-benzoquinone was formed in this or in the previous oxidation. Rapid addition of aniline (1) or 2,5-dimethoxy-4-t-butylaniline to the ether immediately after oxidation gave no other products.

Characterisation of 2,2′-*Diamino*-4,4′-*dimethoxy*-5,5′-*di*-*t*-*butylazobenzene* (29).—(a) *Reductive acetylation.* With zinc dust, sodium acetate, and acetic anhydride in refluxing ether, the azobenzene (29) gave a near quantitative yield of *NN*′-diacetyl-5-methoxy-4-t-butyl-1,2-phenylenediamine.

(b) *Deamination.* The azobenzene (29) (96 mg) was diazotised in methanolic sulphuric acid. Excess of sodium hypophosphite was added to the suspension of the diazon-

[37] J. Burgers, W. van Hartingsveldt, J. van Keulin, P. E. Verkade, H. Visser, and B. M. Wepster, *Rec. Trav. chim.*, 1956, **75**, 1327.

ium salt and the mixture was stirred for 16 h. Basification with ammonia gave a yellow precipitate, which, after evaporation of methanol and addition of water, was filtered off and recrystallised from ether. The first crop of crystals (8 mg) was identical with 4,4′-dimethoxy-3,3′-di-t-butylazobenzene, synthesised as follows.

Addition of diazotised 4-methoxy-3-t-butylaniline to 2-t-butylphenol in ice-cold aqueous sodium hydroxide gave yellow-orange prisms, m.p. 155—156° (from light petroleum–ether) of *4-hydroxy-4′-methoxy-3,3′-di-t-butylazobenzene* (Found: C, 73·9; H, 8·5. $C_{21}H_{28}N_2O_2$ requires C, 74·1; H, 8·3%). Methylation of this in acetone with dimethyl sulphate gave *4,4′-dimethoxy-3,3′-di-t-butylazobenzene*, yellow plates, m.p. 217·5—218·5° (from chloroform) (Found: C, 74·2; H, 8·5; N, 8·2. $C_{22}H_{30}N_2O_2$ requires C, 74·5; H, 8·5; N, 7·9%), $\lambda_{max.}$ ($CHCl_3$) 262, 359sh, 375, and 452sh nm (log ε 3·95, 3·99, 4·02, and 3·44).

5-Methoxy-2-(3-methoxy-4-t-butylanilino)-4-t-butylaniline (26).—Potassium iodide (24·0 g) in water (30 ml) was added slowly with stirring to a solution of the diazonium salt obtained by diazotisation of 4-methoxy-2-nitro-5-t-butylaniline (13·44 g) in acetic acid (300 ml) and water (60 ml) with sodium nitrite (10·8 g) in water (30 ml). After stirring at room temperature for 90 min and heating on a steam-bath for 30 min, the cooled suspension was added to ice-cold sodium disulphite (2%; 600 ml). The precipitate was filtered off and recrystallised from ether giving *2-iodo-5-methoxy-1-nitro-4-t-butylbenzene* as yellow plates (17·8 g, 90%), m.p. 138—139° (Found: C, 39·85; H, 4·4; I, 36·7. $C_{11}H_{14}INO_3$ requires C, 39·45; H, 4·2; I, 37·9%). Chromatography of the mother liquors afforded *2-methoxy-4-nitro-1-t-butylbenzene* (70 mg) as pale yellow prisms, m.p. 77·5—78·5° (from light petroleum) (Found: C, 63·5; H, 7·1; N, 7·0. $C_{11}H_{15}NO_3$ requires C, 63·1; H, 7·2; N, 6·7%). On reduction followed by acetylation this material gave 3-methoxy-4-t-butylacetanilide.

2-Iodo-5-methoxy-1-nitro-4-t-butylbenzene (16·76 g) and 3-methoxy-4-t-butylacetanilide (2) (8·85 g) were heated with copper powder (0·32 g) and potassium carbonate (5·0 g) for 2·5 h in refluxing γ-picoline (150 ml). The mixture was poured into water and extracted with ether. The extracts were washed exhaustively with water, dried, and evaporated to leave a dark crystalline residue, which on recrystallisation from ethanol afforded *N-(3-methoxy-4-t-butylphenyl)-N-(4-methoxy-2-nitro-5-t-butylphenyl)acetamide* (13·45 g, 76%) as pale yellow prisms, m.p. 168—170° (Found: C, 67·1; H, 7·55. $C_{24}H_{32}N_2O_5$ requires C, 67·3; H, 7·5%), τ 2·54 (ArH), 2·62—3·13 (m, 4 × ArH), 6·08 and 6·19 (2 × OMe), 7·93 (COMe), and 8·62 and 8·65 (2 × Bu^t). Unchanged acetanilide (2) (590 mg) was recovered from the mother liquors, and small amounts of 3-methoxy-4-t-butylnitrobenzene and the iodobenzene were detected in the filtrate by t.l.c.

The *NN*-disubstituted acetamide (4·28 g) was heated with potassium hydroxide (1 g) in refluxing dry ethanol for 12 h. Processing in the usual way afforded *4-methoxy-N-(3-methoxy-4-t-butylphenyl)-2-nitro-5-t-butylaniline* in 94% yield as fine orange needles m.p. 116—117·5° (from methanol) (Found: C, 68·6; H, 7·8. $C_{22}H_{30}N_2O_4$ requires C 68·4; H, 7·8%). Steam distillation of the mother liquors from the crystallisation gave *4-methoxy-2-nitro-5-t-butylphenol* (60 mg) as pale yellow needles m.p. 61—61·5° (from light petroleum) (Found: C, 59·0; H, 6·75. $C_{11}H_{15}NO_4$ requires C 58·65; H, 6·7%), $\nu_{max.}$ 3226m cm^{-1}, τ −0·79 (OH), 2·62 and 3·0 (2 × ArH), 6·10 (OMe), and 8·62 (Bu^t).

Hydrogenation of the nitroaniline in ether over 10% palladium–charcoal and anhydrous sodium sulphate gave the *diamine* (26) (88%) as fine needles, m.p. 118—120° (from light petroleum) (Found: C 74·0; H, 9·1; N, 7·8. $C_{22}H_{32}N_2O_2$ requires C, 74·1; H, 9·05; N, 7·9%).

Attempted Preparation of the Diamine (26) *from 3 3′-Dimethoxy-4 4′-di-t-butylazobenzene* (4).—A suspension of the azobenzene (4) (354 mg) in ethanol (150 ml) containing concentrated hydrochloric acid (1 ml) was hydrogenated over 10% palladium–charcoal until the azo-compound had dissolved (24 h). The filtered solution was concentrated under reduced pressure to 20 ml, poured into water (150 ml) containing sodium carbonate (0·6 g), and then extracted with ether. The extracts were washed with water, dried and evaporated to leave an orange gum (354 mg) which crystallised from light petroleum to give *2,2′-diamino-4,4′-dimethoxy-5,5′-di-t-butylbiphenyl* (25) (110 mg) as small prisms, m.p. 100—102° (Found: C, 74·4; H, 9·1; N, 7·7. $C_{22}H_{32}N_2O_2$ requires C, 74·1; H, 9·05; N, 7·9%), τ 2·97 (2 × ArH), 3·66 (2 × ArH), 6·16 (2 × OMe), 6·44 (2 × NH_2), and 8·64 (2 × Bu^t). The *NN′-diacetamide* crystallised as fine needles, m.p. 253—255° (from methanol) (Found: C, 70·8; H, 8·1. $C_{26}H_{36}N_3O_4$ requires C, 70·9; H, 8·2%). A further 6 mg of the biphenyl (25) was obtained from the concentrated mother liquors. Chromatography of these on silicic acid gave 3-methoxy-4-t-butylaniline (210 mg) and a trace of the diamine (26), which was shown to be present by t.l.c.

Oxidation of the Diamine (26).—(a) *By potassium ferricyanide.* Slow dropwise addition of the diamine (460 mg) in light petroleum (250 ml) to a stirred solution of potassium ferricyanide (1·9 g) and sodium hydroxide (0·12 g) in deoxygenated water (500 ml) at room temperature under nitrogen gave a red organic solution, which after stirring for 12 h, was separated from the aqueous phase, washed with water to neutrality, dried, and evaporated under reduced pressure to leave a red gum. This yielded, after chromatography on alumina and refractionation, the phenazines (5) (22 mg) and (6) (*ca.* 1 mg), and the amino-quinone imine (9) (138 mg). T.l.c. showed that the major product before chromatography was the maroon material believed to be 3-methoxy-6-(3-methoxy-4-t-butylphenylimino)-4-t-butylcyclohexa-2,4-dien-1-imine (27), whereas the amino-quinone imine (9) was formed during chromatography.

(b) *By silver oxide.* Oxidation of the diamine (26) (460 mg) with silver oxide (1·5 g) in ether (250 ml) over anhydrous sodium sulphate during 2·75 h at 0° gave the same products (5) (23 mg), (6) (*ca.* 1 mg), and (9) (179 mg). Traces of yellow material of high R_F value and much diimine (27) were detected by t.l.c. before chromatography. No marked increase in the yield of the phenazines was obtained when the oxidation was conducted for 72 h.

(c) *By nitrobenzene.* A gently refluxing solution of the diamine (26) (36 mg) in nitrobenzene (15 ml) under nitrogen during 24 h afforded, after removal of the nitrobenzene by steam distillation and chromatography of the residue on alumina, the phenazines (5) (11 mg) and (6) (trace).

Characterisation and Reactions of 3-Methoxy-6-(3-methoxy-4-t-butylphenylimino)-4-t-butylcyclohexa-2,4-dien-1-imine (27).—Attempted crystallisation of the maroon gum, separated, by preparative t.l.c. on alumina in benzene from the other oxidation products, resulted in the formation of green, purple, and brown materials. The purified gum had $\nu_{max.}$ 3165m and 1615m cm^{-1}, τ 2·93 (vinylic H), 3·60—3·88 (m, 3 × ArH, 1 vinylic H), 6·17 and 6·21 (2 × OMe), and 8·62 and 8·80 (2 × Bu^t).

(a) *Reduction.* Hydrogenation of the crude residue from silver oxide oxidation of the diamine (26) (460 mg) over 10% palladium–charcoal in methanol (30 ml) at 0° was very rapid. Removal of solvent from the filtered solution left a residue which was crystallised from petroleum to give the diamine (26) (360 mg).

(b) *Comparative t.l.c.* A sample of maroon material from the oxidation of aniline (1) by silver oxide, and a sample of (27) from the oxidation of (26) by silver oxide were applied separately to an alumina plate. The plate was exposed to the atmosphere for 24 h and then developed in benzene–chloroform (5 : 1). Small amounts of the phenazine (5), the diamine (26), the amino-quinone imine (9), and orange material of R_F *ca.* 0 were evident. Identical behaviour was observed for each sample. Similar treatment of the diamine (26) also gave (5) and the orange material.

(c) *Cyclisation.* The crude di-imine (27) (30 mg) was heated slowly in nitrobenzene (10 ml). At about 90° the colour of the solution changed from red to brownish yellow, and t.l.c. indicated the presence of substantial quantities of the phenazine (5). After 18 h boiling under reflux the nitrobenzene was removed by steam distillation, and the residue was chromatographed to give a mixture of the phenazines (5) and (6) (26 mg and 17 mg from successive reactions).

In another reaction, treatment of the crude di-imine (27) in boiling ether with acetic acid gave traces of the amino-quinone imine (9) and water-soluble orange material. Attempted oxidative cyclisation with iron(III) chloride in methanol under a variety of conditions was fruitless.

(d) *Condensation with 3-methoxy-4-t-butylaniline* (1). Oxidation of the diamine (26) (95 mg) in the presence of the aniline (1) (45 mg) in ether (60 ml) by silver oxide over anhydrous sodium sulphate during 2 h gave the oxidation products of the diamine. Acetic acid (3 drops) was added to the filtered solution, which was then evaporated to 30 ml under reduced pressure. This solution was set aside overnight, then evaporated, and the residue was chromatographed on silicic acid. Elution with light petroleum–ether (19 : 1) gave material which was rechromatographed to give the di-imine (10) (18 mg).

In another experiment a solution in light petroleum of the crude di-imine (27) (30 mg) and the aniline (1) (100 mg) was applied to neutral alumina. Light petroleum–ether (4 : 1) eluted the blue compound (11); the fraction eluted by light petroleum–ether (7 : 3), which consisted of compounds (1) and (11) was recycled to give more of (11) (9 mg in all). Elution with more polar solvents gave the amino-quinone imine (9), which when subjected to the same process did not react with the aniline (1).

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