

The Chemistry of *ortho*-Benzoquinones. Part VI.¹ The Reaction of Primary Aromatic Amines with Alkyl Substituted 1,2-Benzoquinones: The Displacement of Alkyl Groups in the 4- and 5-Positions

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The reaction of primary aromatic amines with alkyl substituted 1,2-benzoquinones has been investigated. An alkyl substituent in the 3-position has no effect on the course of the reaction which proceeds as with 1,2-benzoquinone itself (see Part IV),² but primary alkyl groups in the 4(5)-position are displaced by an arylamino-group. If there are methyl groups in both the 4- and the 5-positions only one is displaced. The methyl group in 4-methyl-1,2-naphthoquinone is likewise displaced. With *ortho*-phenylenediamine no alkyl displacement occurs but alkyl phenazines are formed. The mechanism of the displacement has been elucidated.

In Part IV² we described the reaction of primary aromatic amines with 1,2-benzoquinone (Ia) and reported that the course of the reaction depended on the nature of the solvent. In methanol solution 4,5-diarylamino-1,2-benzoquinone (IIa) was the predominant

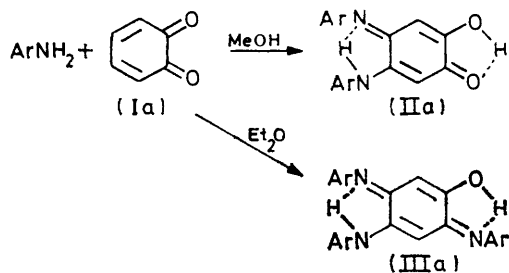
product while in ether 2,5-diarylamino-1,4-benzoquinone mono-anil (IIIa) was the predominant product. When the reaction between 3-methyl-1,2-benzoquinone and primary aromatic amines was investigated similar products (IIb) were obtained in methanol, while in ether 4(5)-arylamino-3-methyl-1,2-benzoquinone was obtained in addition to (IIIb or c).

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¹ Part V, W. M. Horspool, P. I. Smith, and J. M. Tedder, *J. Chem. Soc. (C)*, 1971, 1638.

² W. M. Horspool, P. I. Smith, and J. M. Tedder, *J. Chem. Soc. (C)*, 1971, 138.

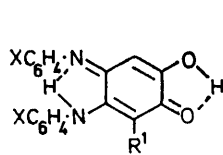
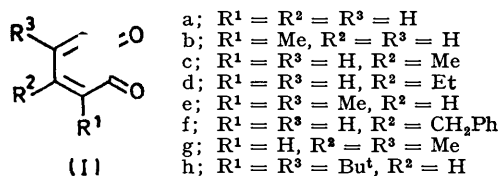
Extension of the study to the reaction of arylamines with 4-methyl-1,2-benzoquinone in methanol yielded 2,5-diarylamino-1,4-benzoquinone mono-anil (IIIa)



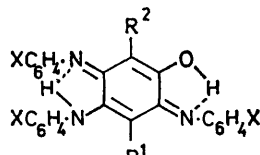
identical to the product obtained by treating 1,2-benzoquinone with the same amine in ether. The observations prompted a more thorough investigation of the reaction of alkyl-1,2-benzoquinones with aromatic amines. The results of this investigation are tabulated below.

Reaction of alkyl-1,2-benzoquinones with arylamines in methanol

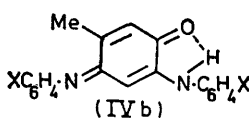
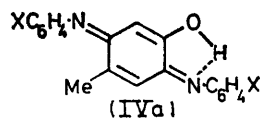
Quinone	Amine	Product
(Ia)	$\text{C}_6\text{H}_5\text{NH}_2$	(IIa; X = H)
(Ia)	$p\text{-ClC}_6\text{H}_4\text{NH}_2$	(IIa; X = Cl)
(Ia)	$p\text{-BrC}_6\text{H}_4\text{NH}_2$	(IIa; X = Br)
(Ia)	$p\text{-MeOC}_6\text{H}_4\text{NH}_2$	(IIa; X = MeO)
(Ib)	$p\text{-MeOC}_6\text{H}_4\text{NH}_2$	(IIb; X = MeO)
(Ic)	$\text{C}_6\text{H}_5\text{NH}_2$	(IIIa; X = H)
(Ic)	$p\text{-ClC}_6\text{H}_4\text{NH}_2$	(IIIa; X = Cl)
(Ic)	$p\text{-MeOC}_6\text{H}_4\text{NH}_2$	(IIIa; X = MeO)
(Id)	$p\text{-MeOC}_6\text{H}_4\text{NH}_2$	(IIIa; X = MeO)
(Ie)	$p\text{-MeOC}_6\text{H}_4\text{NH}_2$	(IIIb; X = MeO)
(Ie)	$p\text{-ClC}_6\text{H}_4\text{NH}_2$	(IIIc; X = MeO)
(Ie)	$p\text{-ClC}_6\text{H}_4\text{NH}_2$	(IIIb; X = Cl)
(Ie)	$p\text{-ClC}_6\text{H}_4\text{NH}_2$	(IIIc; X = Cl)
(If)	$p\text{-MeOC}_6\text{H}_4\text{NH}_2$	(IIIa; X = MeO)
(Ig)	$p\text{-ClC}_6\text{H}_4\text{NH}_2$	(IVa or IVb; X = Cl)
(Ig)	$p\text{-MeOC}_6\text{H}_4\text{NH}_2$	(IVa or IVb; X = MeO)



a; $\text{R}^1 = \text{H}$
 b; $\text{R}^1 = \text{Me}$

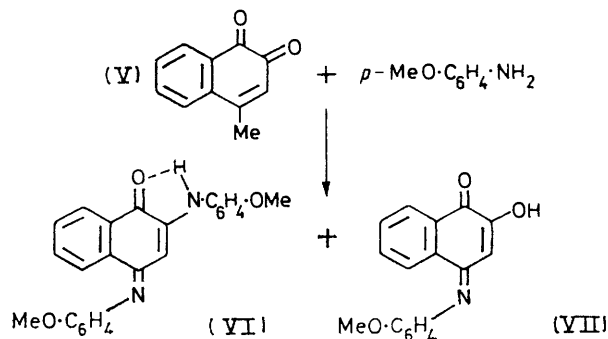


a; $\text{R}^1 = \text{R}^2 = \text{H}$
 b; $\text{R}^1 = \text{Me}, \text{R}^2 = \text{H}$
 c; $\text{R}^1 = \text{H}, \text{R}^2 = \text{Me}$



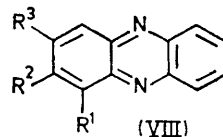
4-Methyl-1,2-naphthoquinone (V) treated with *p*-anisidine in methanol gave two products (VI) and

(VII) both of which involve methyl displacement. Product (VII) could theoretically be derived from (VI) by hydrolysis but it was found that (VII) could not be hydrolysed under conditions far more vigorous than those employed in the reaction, so that in this case methyl displacement precedes or occurs concurrently with anil formation.



The first feature to notice about the tabulated results is that only alkyl groups *para* to a carbonyl group in the starting quinone are displaced. Secondly, when there are two such groups [*i.e.* in 4,5-dimethyl-1,2-benzoquinone (Ig)] only one is displaced. Thirdly, when a displacement occurs with a benzoquinone the product is the 2,5-diarylamino-1,4-benzoquinone mono-anil (III) even though the reaction is carried out in methanol (*cf.* Part IV).² An ethyl group [*e.g.* (Id)] is displaced just as readily as a methyl group. However in an experiment with 3,5-di-*t*-butyl-1,2-benzoquinone (Ih) no displacement occurred. The nature of the product from this reaction is discussed below.

In Part IV we have described how *ortho*-phenylenediamine reacts with 1,2-benzoquinone (Ia) in methanol to yield 2,3-dihydroxyphenazine (VIIIa) but in ether gave poor yields of phenazine itself (VIIIb). When either 3,5-dimethyl-1,2-benzoquinone (Ie) or 4,5-dimethyl-1,2-benzoquinone (Ig) was treated with *ortho*-phenylenediamine in methanol they yielded phenazines (VIIIc) and (VIIId) respectively. 4-Methyl-1,2-benzoquinone (Ic) treated with *ortho*-phenylenediamine in methanol yields 2-(2-aminophenyl)amino-3-methylphenazine (VIIIe). No evidence could be found for methyl displacement or ring closure on to the methyl group.

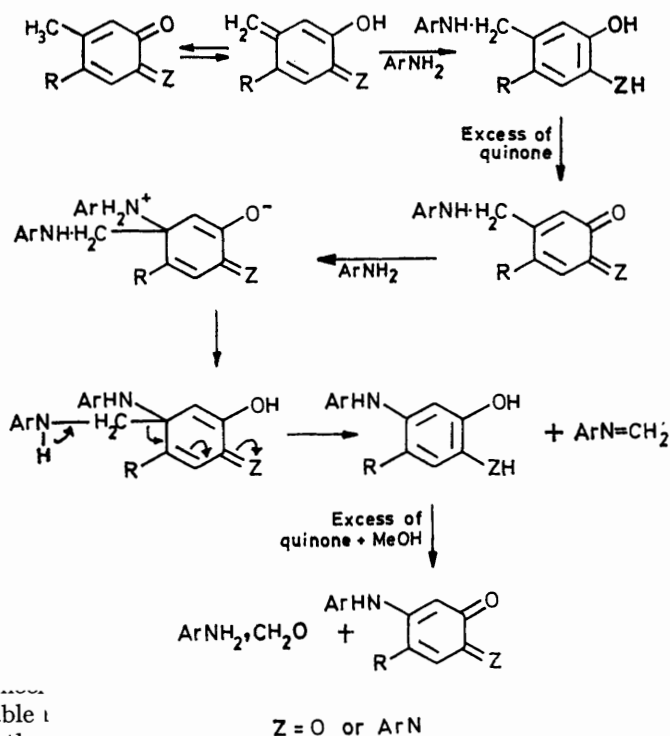


a; $\text{R}^1 = \text{H}, \text{R}^2 = \text{R}^3 = \text{OH}$
 b; $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$
 c; $\text{R}^1 = \text{R}^2 = \text{Me}, \text{R}^3 = \text{H}$
 d; $\text{R}^1 = \text{H}, \text{R}^2 = \text{R}^3 = \text{Me}$
 e; $\text{R}^1 = \text{H}, \text{R}^2 = \text{Me}, \text{R}^3 = o\text{-NH}_2\text{-C}_6\text{H}_4\text{NH}_2$

As far as we are aware there has been no previous report of alkyl displacement from an *ortho*-quinone, although as we shall see below displacements of this kind have been known with *para*-quinones for many years. In order to elucidate the mechanism the effect of atmospheric oxygen and solvent were investigated. When the reaction between 1,2-benzoquinone and

p-anisidine was carried out in a vacuum line using degassed solvents and reactants, the same products were obtained, in other words atmospheric oxygen is not involved. When the reaction of *p*-anisidine was carried out in ether with 4-methyl-1,2-benzoquinone (Ic) the same product (IIIa; X = OMe) was obtained (as was isolated from the reaction of *p*-anisidine and 1,2-benzoquinone) although the yield was less than in methanol. This suggests that the solvent plays no direct part in the reaction but that solvation, probably of the transition state, is important. From the results with *ortho*-phenylenediamine it appears that the first reaction of 3,5-dimethyl- or 4,5-dimethyl-1,2-benzoquinone with a mono-amine will be addition to the carbonyl even in methanol.

We believe the dealkylation involves the addition of the arylamine to a quinone methide or a quinone imine methide. This results in the formation of an arylamino-methyl group (ArNHCH₂) which is a more likely leaving group than a methyl. The steps in the reaction would then be as follows, as shown in the scheme, with Z being either an oxygen atom or an arylimino-group (ArN=).



able
methy

It was not possible to prove the presence of formaldehyde in the reaction mixture, but it could be detected in the solvent which had been distilled off after the reaction. If the above mechanism is correct then the possibility of forming a bis(arylamino)methyl group

must be considered. However the leaving group would now be the carbodi-imide (rN=C=NAr) and the final product would be the *N*,*N*-diarylurea which was not detected. The reactivity of 4-ethyl-1,2-benzoquinone and the failure of 3,5-di-*t*-butyl-1,2-benzoquinone to undergo displacement are all consistent with the proposed mechanism.

The literature gives some support to our proposed mechanism. Displacement of alkyl groups in *para*-quinones has been known for a long time. Hoffmann³ reported the displacement of the methyl group in 2,5-dibromo-3-isopropyl-6-methyl-1,4-benzoquinone by aniline and the reaction was further investigated by Bötters⁴ in the following year. Anslow and Raistrick⁵ reported the displacement of the methyl from 4-methoxy-toluquinone. These results were later discussed by Smith, Arnold, and Nichols⁶ and again by Bunnett and Zahler⁷ in their comprehensive review of nucleophilic substitution. Very much more recently Cameron and Scott⁸ reported the replacement of one methyl group from 3,5-dimethyl-1,4-benzoquinone by methylamine. As far as we are aware there are no previous reports of displacements from *ortho*-quinones. From a mechanistic point of view, much more significant is the side-chain amination of alkyl *para*-quinones observed by Cameron, Scott, and Todd⁹ using conditions very similar to those used in the present work. The fact that their reaction stopped at the aminoalkylquinone stage in most cases may be due to the fact that their aminoalkyl group is *ortho*- to the carbonyl group whereas in our case the activating group is *para*. Cameron and Scott⁸ postulate loss of the aminated side-chain followed by nucleophilic attack at the resultant unsubstituted position. This would represent a 'reverse Mannich' reaction. Neither they nor the present workers detected any of the dealkylated product and a 'reverse Mannich' seems unlikely under the conditions employed. We therefore prefer our proposal which involves nucleophilic substitution. However both mechanisms may occur depending on the reaction conditions, the 'reverse Mannich' being more likely in acidic media.

In order to verify our mechanism we attempted to isolate the anil formed. Unfortunately we were unsuccessful in separating the formaldehyde anil from the unchanged *p*-anisidine. We therefore synthesised 4-benzyl-1,2-benzoquinone (If) and treated it with *p*-anisidine in methanol. This yielded the expected 2,5-diarylamino-1,4-benzoquinone mono-anil (IIIa; X = MeO) together with benzylidene-*p*-anisidine in equimolecular amounts.

In this case therefore our proposed mechanism is established. Although we have been unable to isolate the formanil in experiments in which a methyl group is displaced we have been able to detect formaldehyde when the reaction mixture is hydrolysed with acid.

³ J. Hoffmann, *Ber.*, 1901, **34**, 1558.

⁴ O. Bötters, *Ber.*, 1902, **35**, 1502.

⁵ W. K. Anslow and H. Raistrick, *J. Chem. Soc.*, 1939, 1446.

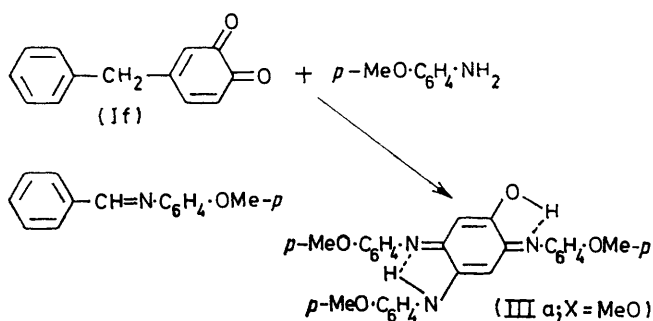
⁶ L. I. Smith, R. T. Arnold, and J. Nichols, *J. Amer. Chem. Soc.*, 1943, **65**, 2131.

⁷ J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, 1951, **49**, 273.

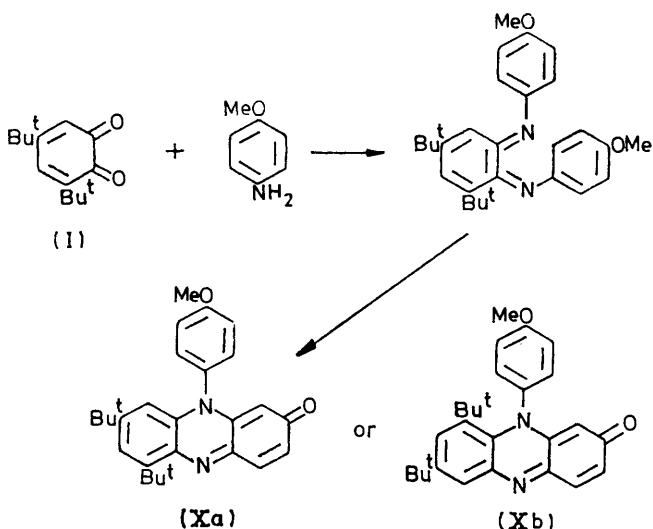
⁸ D. W. Cameron and P. M. Scott, *J. Chem. Soc.*, 1964, 5569.

⁹ D. W. Cameron, P. M. Scott, and Lord Todd, *J. Chem. Soc.*, 1964, 42.

There seems every justification therefore for concluding that the same mechanism applies in these cases.



The failure of 3,5-di-*t*-butyl-1,2-benzoquinone (Ih) to undergo an alkyl displacement reaction has been mentioned. However this quinone did react with *p*-anisidine to give a different type of adduct, in which both arylamino-residues added to the carbonyl groups. This is the only case in which we have found evidence for the formation of a 1,2-dianilinoquinone. The formation of this product (X) is probably the result of cyclisation and oxidation of the initial 1,2-dianil. Several mechanistic rationalisations for the formation of this compound (X) can be put forward but the exact details have not been determined. Structure (Xa) is preferred to the alternative (Xb) firstly on steric grounds (molecular models



indicate that it is almost impossible to construct the other isomer) and secondly on the basis of n.m.r. studies. At room temperature the *t*-butyl group protons resonate at τ 8.55 as a broad singlet and at τ 8.65 as a sharp singlet but at 60° the broad τ 8.55 absorption sharpens to a peak identical to the absorption at τ 8.65. This shows that the peak broadening is due to hindered rotation and not to a Nuclear Overhauser Effect (such an effect would be expected due to the proximity of the

aryl protons on N-1 and the *t*-butyl group on C-10 in the other isomer). A decoupling experiment with both the aromatic protons and the broadened *t*-butyl group confirmed the absence of a Nuclear Overhauser Effect.

EXPERIMENTAL

Fremy's salt was prepared by the method of Harvey and Hollingshead.¹⁰ 3-Methyl-1,2-benzoquinone (Ib), 4-methyl-1,2-benzoquinone (Ic), and 4-benzyl-1,2-benzoquinone (If) were prepared by oxidation of the corresponding catechol by tetrachloro-1,2-benzoquinone in dry ether at -25° . 4,5-Dimethyl-1,2-benzoquinone (Ig) (m.p. $85\text{--}86^\circ$, lit.,¹¹ m.p. 106°) 3,5-dimethyl-1,2-benzoquinone (Ic), 4-ethyl-1,2-benzoquinone (Id) and 3,5-di-*t*-butyl-1,2-benzoquinone (Ih) (m.p. $111\text{--}112^\circ$, lit.,¹² m.p. 113°) were prepared by Fremy's salt oxidation of the corresponding alkyl phenol. The quinones were all stored at Cardice temperatures and were usually used without further purification.

Preparation of 4-Benzylcatechol.—3,4-Dimethoxybenzophenone (m.p. $98\text{--}100^\circ$, lit.,¹³ m.p. 99°) was reduced with zinc amalgam to 3,4-dimethoxybenzylbenzene which was then demethylated with the HBr in acetic acid to yield 4-benzylcatechol (as fine colourless needles from benzene-light petroleum), m.p. $91\text{--}92^\circ$ (Found: C, 78.1; H, 6.2. Calc. for $\text{C}_{13}\text{H}_{12}\text{O}_2$: C, 78.0; H, 6.0%).

Preparation of 4-Methyl-1,2-naphthoquinone (V).—4-Methyl-2-amino-1-naphthol (3.4 g; prepared by the method of Fieser¹⁴) was dissolved in water (1.5 l) containing conc. hydrochloric acid (6 ml). Ferric chloride (14.4 g) in water (90 ml) and conc. HCl (3 ml) was added in one lot. Yellow crystals of the quinone (3.14 g) which precipitated, were collected and dried in a desiccator.

Reaction of 3-Methyl-1,2-benzoquinone (Ib) with p-Anisidine in Methanol.—A solution of *p*-anisidine (1.85 g) in methanol (10 ml) was added to a solution of 3-methyl-1,2-benzoquinone (0.61 g) in the same solvent (10 ml). The mixture was stirred for several minutes and then allowed to stand for 24 h, with occasional stirring. The crude product (0.46 g) was filtered off and was crystallised from methanol to give dark, shiny, needle-like crystals of 4,5-di-(*p*-methoxyanilino)-3-methyl-1,2-benzoquinone (IIb), m.p. 142° ; ν_{max} (Nujol) 3320, 1670m, 1610s, and 1570 cm^{-1} ; λ_{max} (CHCl_3) 464 (ϵ 1.9×10^4), 304 (1.66×10^4), 255sh, and 240 nm (1.9×10^4). The mass spectrum showed major ions at m/e 364 (M^+), 363, 349, 333, 123 and 108; $\tau(\text{CDCl}_3)$ 3.07 (m, 10H), 3.92 (s, 1H), 6.2 (s, 6H), and 8.42 (s, 3H) (Found: C, 69.1; H, 5.6; N, 7.6. $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_4$ requires C, 69.2; H, 5.5; N, 7.7%).

The original methanol filtrate was evaporated to dryness and the solid residue was chromatographed on alumina. Only *p*-anisidine (1.06 g) was identified.

Reactions of 3-Methyl-1,2-benzoquinone (Ib) with p-Anisidine in Ether.—A mixture of 3-methyl-1,2-benzoquinone (2.27 g) and *p*-anisidine (2.26 g) was taken into a minimum quantity of dry ether and stirred overnight. The crude product (1.0 g) was filtered off and recrystallised from methanol to give dark, needle-like crystals of 4(or 5)-*p*-methoxyanilino-3-methyl-1,2-benzoquinone, m.p. $>360^\circ$, ν_{max} (Nujol) 3160, 1675, 1655, 1620, 1595, 1275, and 1260 cm^{-1} ; λ_{max} (CHCl_3) 508 (ϵ 4.86×10^3), 366 (4.92×10^3), 268sh, and 242 nm (1.15×10^4); mass spectrum shows ions

¹² W. Flaig, T. Ploetz, and H. Biergmans, *Annalen*, 1955, **597**, 196.

¹³ Fr. Brüggeman, *J. prakt. Chem.*, 1896, **53**, 253.

¹⁴ L. F. Fieser, *Org. Synth.*, 1943, vol. II, 35.

¹⁰ G. H. Harvey and R. G. W. Hollingshead, *Chem. and Ind.*, 1953, 244.

¹¹ H.-J. Teuber and G. Staiger, *Chem. Ber.*, 1955, **88**, 802.

at m/e 245 ($M + 2$), 243 (M^+), 230, 228, and 200 (Found: C, 68.7; H, 5.4; N, 5.8. $C_{14}H_{13}NO_3$ requires C, 69.1; H, 5.4; N, 5.8%).

In another experiment, the solvent was stripped from the filtrate to give a brown oil. This was taken into chloroform and chromatographed on alumina. *p*-Anisidine was isolated together with the mono-*p*-methoxyanil of 2,5-di-(*p*-methoxyanilino)-3(or 6)-methyl-1,4-benzoquinone [(IIIb) or (IIIc)]. The i.r. and mass spectra of this compound were identical to those of a sample prepared from 3,5-dimethyl-1,2-benzoquinone. The melting points of the two samples were identical and unchanged on taking a mixture.

Reaction of 4-Methyl-1,2-benzoquinone (Ib) with Aniline.—A solution of 4-methyl-1,2-benzoquinone (Ib) (3.0 g) in methanol (25 ml) was added to a solution of freshly distilled aniline (4.6 g) in the same solvent (25 ml). The mixture was set aside for 4 days and then filtered to yield the mono-anil of 2,5-dianilino-1,4-benzoquinone (IIA; X = H) (1.61 g). The solvent was stripped from the filtrate to give a brown oil. This was taken into a little chloroform and chromatographed on a silica-gel column. A further 1.86 g of the anil was obtained together with a brown oil consisting (t.l.c. on silica gel) of several components. This was chromatographed on an alumina column to give aniline (1.17 g) as the only product which could be identified.

The crude anil was recrystallised from chloroform to give dark fluffy crystals. The i.r. spectrum and melting point and mixed melting point were identical to those of an authentic sample.

Reaction of 4-Methyl-1,2-benzoquinone (Ib) with *p*-Chloroaniline.—A solution of *p*-chloroaniline (6.35 g) in methanol (20 ml) was added to a solution of 4-methyl-1,2-benzoquinone (Ib) in the same solvent (40 ml). The flask was stoppered and then set aside for 2 weeks. The crude product (1.68 g) was filtered off and recrystallised from chloroform to give fine red-brown crystals of the mono-*p*-chloroanil of 2,5-di-(*p*-chloroanilino)-1,4-benzoquinone (IIA; X = Cl) whose m.p. 239° and mixed m.p. with an authentic sample were identical; its i.r. and mass spectra were also identical to those of an authentic sample. The solvent was stripped from the filtrate under reduced pressure to give a brown semisolid. This was taken into chloroform and chromatographed on silica gel. The only product which could be identified was *p*-chloroaniline (2 g).

Reaction of 4-Methyl-1,2-benzoquinone (Ib) with *p*-Anisidine in Methanol.—A solution of 4-methyl-1,2-benzoquinone (Ib) (0.64 g) in methanol (5 ml) was added to a solution of *p*-anisidine (2.45 g) in the same solvent (5 ml). The mixture was set aside for 3 days. The crude product (1.03 g) was filtered off and recrystallised from chloroform to give the dark brown mono-*p*-methoxyanil of 2,5-di-(*p*-methoxyanilino)-1,4-benzoquinone (IIA; X = OMe), m.p. and mixed m.p. 201°. The i.r. and mass spectra were identical to those of an authentic sample.

The solvent was stripped from the filtrate obtained from the isolation of the product to give a green oil. This was diluted with chloroform and chromatographed on alumina. The only product identified was *p*-anisidine (1.21 g).

Reaction of 4-Methyl-1,2-benzoquinone (Ib) with *p*-Anisidine in Ether.—A solution of *p*-anisidine (2.57 g) in dry ether (50 ml) was added to a solution of 4-methyl-1,2-benzoquinone (Ib) (0.61 g) in 50 ml of the same solvent. The mixture was shaken and then set aside for 2 days. The crude product (0.25 g) was filtered off and the solvent was stripped from the filtrate under reduced pressure to give a

red oil. This was diluted with chloroform and chromatographed on alumina to give *p*-anisidine (2.22 g) as the only fraction which could be identified. The crude product was recrystallised from chloroform to give the dark brown mono-*p*-methoxyanil of 2,5-di-(*p*-methoxyanilino)-1,4-benzoquinone (IIA; X = OMe), m.p. and mixed m.p. 201°. The mass and i.r. spectra were identical to those of an authentic sample.

Reaction of 4-Methyl-1,2-benzoquinone (Ib) with *o*-Phenylenediamine.—A mixture of 4-methyl-1,2-benzoquinone (Ib) (2.44 g) and *o*-phenylenediamine (4.32 g) in methanol (50 ml) was set aside for 24 h. The red-brown solid (0.51 g) which precipitated was filtered off and recrystallised from methanol to give 2-(2-aminophenyl)-amino-3-methylphenazine (VIIIE) as an orange solid, m.p. >360°; ν_{\max} (Nujol) 3190, 1620, 1610, 1599, 1565, 1545, 765, and 740 cm^{-1} ; the mass spectrum showed ions at m/e 300 (M^+) 285, 194, 150, and 142 (measured mol. wt. 300.1374. $C_{19}H_{16}N_4$ requires 300.1375). The solvent was stripped from the filtrate under reduced pressure to give a brown solid. This was taken into a mixture of pyridine (10 ml) and acetic anhydride (10 ml). The resultant solution, which heated to boiling spontaneously, was set aside for 24 h. *NN'*-Diacetyl-*o*-phenylenediamine (5.1 g), m.p. 185° (lit.,¹⁵ m.p. 185—186°), crystallised out and was filtered off. The filtrate was poured into ice-water (200 ml) and extracted with chloroform (3 × 200 ml). The extract was washed with dilute hydrochloric acid and dried ($MgSO_4$); the solvent was stripped off to give a red oil which solidified with time. This was dissolved in chloroform and examined by chromatography on a silica-gel column. No identifiable products were isolated.

Reaction of 4,5-Dimethyl-1,2-benzoquinone (Ig) with *p*-Chloroaniline.—A solution of 4,5-dimethyl-1,2-benzoquinone (Ig) (0.7 g) and *p*-chloroaniline (1.3 g) in methanol (10 ml) was set aside for 24 h. The crude product (0.25 g) precipitated and was filtered off and recrystallised from methanol to give dark shiny platelets of the mono-*p*-chloroanil of 4(or 5)-*p*-chloroanilino-5(or 4)-methyl-1,2-benzoquinone (IVA or IVb; X = Cl), m.p. 176°; ν_{\max} (Nujol) 3305, 1650, 1625, 1600, 1587, and 1575 cm^{-1} ; λ_{\max} ($CHCl_3$) 490 (ϵ 6.25 × 10³) and 283 nm (2.34 × 10⁴); τ ($CDCl_3$) 2.6—3.5 (m, 10H), 3.78 (s, 1H), and 7.70 (s, 3H); mass spectrum shows ions at m/e 356 (M^+ for ³⁵Cl), 339 and 321 (Found: C, 63.7; H, 3.8; N, 8.0. $C_{19}H_{14}Cl_2N_2O$ requires C, 63.7; H, 3.8; N, 7.9%).

Reaction of 4,5-Dimethyl-1,2-benzoquinone (Ig) with *p*-Anisidine.—*p*-Anisidine (0.43 g) was added to a solution of 4,5-dimethyl-1,2-benzoquinone (Ig) (0.5 g) in methanol (10 ml). The mixture was stirred until the *p*-anisidine had dissolved and was then set aside for 5 days. The solvent was stripped off from the resultant solution to give a purple solid. This was taken into chloroform and chromatographed on alumina. The only product identified and crystallised from ethanol as shiny purple crystals was the mono-*p*-methoxyanil of 5-*p*-methoxyanilino-4-methyl-1,2-benzoquinone (IVA or IVb; X = OMe) (92 mg), m.p. 138°; ν_{\max} (Nujol) 3320, 1655, and 1520 cm^{-1} ; λ_{\max} ($CHCl_3$) 610inf, 518 (ϵ 6.74 × 10³), and 295inf nm; τ ($CDCl_3$) 2.8—3.7 (m, 11H), 6.25 (d, 6H), and 7.65 (s, 3H); mass spectrum showed ions at m/e 348 (M^+), 333, 331, 317, 226, 123, and 108 (Found: C, 72.9; H, 6.1; N, 8.1. $C_{21}H_{20}N_2O_3$ requires C, 72.4; H, 5.8; N, 8.1%).

¹⁵ 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

Reaction of 4,5-Dimethyl-1,2-benzoquinone (Ig) with o-Phenylenediamine.—A solution of *o*-phenylenediamine (1.08 g) in methanol (10 ml) was added to a solution of 4,5-dimethyl-1,2-benzoquinone (Ig) (1.0 g) in methanol (15 ml). The mixture was set aside overnight before being filtered to yield 2,3-dimethylphenazine as a yellow solid (0.43 g). The solvent was stripped off from the filtrate to give a dark solid which was taken up in pyridine (10 ml). Acetic anhydride (10 ml) was added and the mixture was set aside for 36 h. The *NN'*-diacetyl-*o*-phenylenediamine (0.53 g) which was precipitated was filtered off and recrystallised from benzene; it had m.p. 185–186° (lit.,¹⁵ m.p. 185–186°). The filtrate was poured into ice-water and the mixture was filtered to yield a further 0.34 g of the phenazine. The filtrate was extracted with chloroform (3 × 200 ml) and the extract was washed with dilute hydrochloric acid, dried (MgSO₄) and the solvent stripped off to give a red oil. This was taken into chloroform and examined on a silica-gel column. No identifiable products were isolated.

The 2,3-dimethylphenazine (VIIIId) obtained was recrystallised from methanol to give a pale solid, m.p. 173° (lit.,¹¹ m.p. 173°), ν_{\max} (Nujol) 1500w, 867s, and 755s cm⁻¹. The mass spectrum showed major ions at *m/e* 208 (*M*⁺), 193, 181, 138, 103, 77; τ (CDCl₃) 1.7–2.4 (m, 6H), 7.54 (s, 6H) (measured mol. wt. 208.0997. C₁₄H₁₂N₄ requires 208.1004).

Reactions of 3,5-Dimethyl-1,2-benzoquinone (Ie) with p-Chloroaniline.—A solution of *p*-chloroaniline (2.03 g) in methanol (10 ml) was added to a solution of 3,5-dimethyl-1,2-benzoquinone (Ie) (0.72 g) in the same solvent (10 ml). The flask was stoppered and then set aside for 2 weeks. The crude produce (0.19 g) was filtered off and recrystallised from methanol to give fine needle-shaped crystals of the *mono-p-chloroanil* of 2,5-di-(*p*-chloroanilino)-3(or 6)-methyl-1,4-benzoquinone (IIIb or IIIc; X = Cl), m.p. 210–211°; ν_{\max} (Nujol) 3260, 1620, 1600, and 1580 cm⁻¹; λ_{\max} (CHCl₃) 532sh, 402 (ϵ 1.67 × 10⁴), and 286 nm (3.1 × 10⁴); τ (CDCl₃) 2.6–3.3 (m, 14H), 3.95 (s, 1H), and 8.3 (s, 3H); mass spectrum showed principal ions at *m/e* 481 (*M*⁺ for ³⁵Cl), 445, 343, and 206 (Found: C, 61.7; H, 3.7; N, 8.6. C₂₅H₁₈Cl₃N₃O requires C, 62.2; H, 3.7; N, 8.7%).

Reactions of 3,5-Dimethyl-1,2-benzoquinone (Ie) with p-Anisidine.—A solution of *p*-anisidine (1.58 g) in methanol (5 ml) was added to a stirred solution of 2,5-dimethyl-1,2-benzoquinone (Ie) (0.72 g) in the same solvent (5 ml). The mixture was stirred for 5 min after which a further 10 ml of methanol was added; the flask was then stoppered and set aside for 3 weeks. The crude product (1.32 g) was filtered off and recrystallised from ethanol to give fluffy brown crystals of the *mono-p-methoxyanil* of 2,5-di-(*p*-methoxyanilino)-3(or 6)-methyl-1,4-benzoquinone (IIIb or IIIc; X = OMe), m.p. 176–177°; ν_{\max} (Nujol) 3270, 1630, 1595, 1510, and 1250 cm⁻¹; λ_{\max} (CHCl₃) 550sh, 409 (ϵ 2.41 × 10⁴), 295 inf, 275 (2.41 × 10⁴), and 240 nm (2.07 × 10⁴); mass spectrum shows major ions at *m/e* 471 (*M* + 2), 469 (*M*⁺), 468, 454, 438, 123, and 108; τ (CDCl₃) 2.4–3.3 (m, 14H), 3.9 (s, 1H), 6.25 (two absorptions in ratio of 2 : 1, 9H), and 8.37 (s, 3H) (Found: C, 71.3; H, 5.7; N, 8.7. C₂₈H₂₇N₃O₄ requires C, 71.6; H, 5.7; N, 8.9%).

Reaction of 3,5-Dimethyl-1,2-benzoquinone (Ie) with o-Phenylenediamine.—A solution of *o*-phenylenediamine in methanol (10 ml) was added to a solution of 3,5-dimethyl-1,2-benzoquinone (Ie) (0.68 g) in the same solvent (15 ml). The reaction flask was stoppered and set aside for 2 weeks.

The solution was filtered to produce a trace amount of unidentifiable black solid. The solvent was stripped off from the filtrate to yield a brown oil which was taken into a mixture of pyridine (10 ml) and acetic anhydride (10 ml) and then set aside for 2 days. *NN'*-Diacetyl-*o*-phenylenediamine (0.37 g) was filtered off. The filtrate was poured into ice-water to give 1,3-dimethylphenazine (VIIIc) (1.1 g). This was recrystallised from methanol to yield dark shiny crystals, m.p. 121–122° (lit.,¹¹ m.p. 123°); ν_{\max} (Nujol) 1625w, 1515w, 864s, 840m, and 760s cm⁻¹. The mass spectrum showed major ions at *m/e* 209, 208 (*M*⁺), 207, 193, 181, 103, 91, and 77; τ (CDCl₃) 1.6–2.4 (m, 6H), 7.17 (s, 3H), and 7.46 (s, 3H) (measured mol. wt. 208.0997. C₁₄H₁₂N₂ requires 208.1004).

Reaction of 4-Ethyl-1,2-benzoquinone (Id) with p-Anisidine.—A solution of *p*-anisidine (0.61 g) in methanol (5 ml) was added to a solution of 4-ethyl-1,2-benzoquinone (Id) in the same solvent (5 ml). After 3 h the crude product which had precipitated was filtered off. A further crop of crystals was obtained after 2 days. Examination of the filtrate as before yielded only *p*-anisidine. The crude product was recrystallised from methanol to give the dark brown *mono-p*-methoxyanil of 2,5-di-(*p*-methoxyanilino)-1,4-benzoquinone (IIIa; X = OMe). The i.r. spectrum was identical to that of an authentic sample. The m.p. and mixed m.p. was identical to that of an authentic sample.

Reaction of 4-Benzyl-1,2-benzoquinone (If) with p-Anisidine.—A solution of *p*-anisidine (2.5 g) in methanol (5 ml) was added to a solution of 4-benzyl-1,2-benzoquinone (If) (3.0 g) in the same solvent (10 ml). The mixture was set aside overnight to give a dark precipitate of the *mono-p*-methoxyanil of 2,5-di-(*p*-methoxyanilino)-1,4-benzoquinone (IIIa); this was filtered off and recrystallised from chloroform [0.38 g, m.p. 202°]. The i.r. spectrum was identical to that of the authentic sample.

The solvent was removed from the filtrate to give a brown oil which was diluted with chloroform and chromatographed on an alumina column. Chloroform eluted benzylidene-*p*-anisidine (0.16 g) and *p*-anisidine. The former was recrystallised from ethanol to give colourless platelets, m.p. and mixed m.p. 69°. The i.r. spectrum was identical to that of an authentic sample prepared by the method of Philipp.¹⁶

Reaction of 4-Methyl-1,2-naphthoquinone (V) with p-Anisidine.—A solution of *p*-anisidine (1.23 g) in methanol (5 ml) was added to a suspension of 4-methyl-1,2-naphthoquinone in the same solvent (15 ml). The mixture was stirred until all the quinone had dissolved, the solution slowly becoming scarlet. The mixture was set aside overnight. The purple granular crystals were filtered off and a second crop was recovered from the liquor after 24 h (total recovery 1.25 g). The crude product was taken into chloroform and the solution was examined by t.l.c. on silica gel; it showed the presence of two components. The two products were separated on a silica-gel column. Chloroform-acetone (19:1) eluted the *mono-p-methoxyanil* of 4-*p*-methoxyanilino-1,2-naphthoquinone (VI), m.p. 218–219°; ν_{\max} (Nujol) 3310, 1650, 1590, and 1500 cm⁻¹; λ_{\max} (CHCl₃) 504 (ϵ 6.66 × 10⁴), 330sh, 278 (2.09 × 10⁴), and 252 nm (1.94 × 10⁴); the mass spectrum showed major ions at 384 (*M*⁺), 369, 279, 264, 177, and 149 (measured mol. wt. 384.14738. C₂₄H₂₀N₂O₃ requires 384.14738).

¹⁶ C. Philipp, *Ber.*, 1892, **25**, 3248.

Elution with methanol eluted a small quantity of 4-*p*-methoxyanilino-1,2-naphthoquinone (VII), m.p. 204.5°; ν_{\max} (Nujol) 3200, 1684, 1600, 1580, 1520, and 1500 cm^{-1} ; λ_{\max} (CHCl_3) 474 (ϵ 3.51×10^3), 346 (3.46×10^3), 278 (9.98×10^3), and 244 nm (1.71×10^4) (measured mol. wt. 279.0897. $\text{C}_{17}\text{H}_{13}\text{NO}_3$ requires 279.095).

*Reaction of 3,5-Di-*t*-butyl-1,2-benzoquinone (Ih) with p-Anisidine.*—A mixture of 3,5-di-*t*-butyl-1,2-benzoquinone (0.5 g) and *p*-anisidine (0.33 g) in methanol (10 ml) was set aside overnight. The purple crystals of 10-*p*-methoxyphenyl-6,8-di-*t*-butylphenazin-2-one (Xa) (0.35 g) obtained

were filtered off, m.p. 192.3°; ν_{\max} (Nujol) 1630, 1600, 1570, 1500, and 1250; τ (CDCl_3), 2.5—3.2 (m, 9H), 6.15 (s, 3H), 8.55 (bs, 9H), and 8.65 (s, 9H); the mass spectrum showed major ions at m/e 414 (M^+), 399, 383, 369, 353, 327 (measured mol. wt. 414.231. $\text{C}_{27}\text{H}_{30}\text{N}_2\text{O}_2$ requires 414.231).

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