Estimation of Phenols by the 4-Aminoantipyrine Method: Identification of the Colored Reaction Products by Proton Magnetic Resonance Spectroscopy

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The products from the oxidation of several phenols in the presence of 4-aminoantipyrine have been isolated and their p.m.r. spectra examined. The results confirm the proposed formation of *p*-quinoneimide adducts and the elimination of the para-group in the case of reactive *p*-substituted phenols. Data from ortho-substituted phenols reveal the formation of *syn* and *anti* geometrical isomers of the quinoneimide. In contrast, when the starting phenol has a meta-substituent, only a single isomer, the less hindered *anti* form, is obtained. An unusually large anisotropic effect of the antipyryl group, causing a deshielding of the closest proton on the quinoneimide ring, has been found. In the reaction between *p*-benzoquinone and 4-aminoantipyrine, the color obtained is due to the formation of the *p*-quinoneimide, and not to a charge-transfer complex.

Les produits d'oxydation de plusieurs phénols en présence d'amino-4 antipyrine ont été isolés et leurs spectres de r.m.n. examinés. Les résultats confirment la formation proposée d'adduits de la *p*-quinone imide et l'élimination du groupe para dans le cas des phénols *p*-substitués réactifs. Les données sur les phénols ortho substitués révèlent la formation d'isomères géométriques *syn* et *anti* de la quinoneimide. Au contraire, lorsque le phénol de départ possède un substituant méta, la forme *anti* la moins encombrée est le seul isomère obtenu. On a constaté un effet d'anisotropie inhabituellement fort du groupe antipyryle provoquant un déblindage du proton le plus proche sur le cycle quinone imide. Dans la réaction entre la *p*-benzoquinone et l'amino-4 antipyrine, la couleur observée est due à la formation de la *p*-quinoneimide et non au complexe de transfert de charge. [Traduit par le journal]

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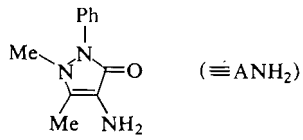
Introduction

The presence of phenols at very low (p.p.b.) concentrations in potable water supplies may cause taste and odor problems on chlorination. The standard procedure (1) for the estimation of phenols at such levels involves the photometric measurement of the dye formed on oxidation of the phenol-containing sample in the presence of excess 4-aminoantipyrine (4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one), **1** (4-AAP). Our



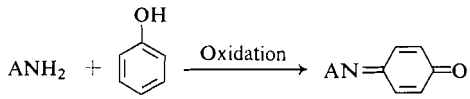
($\equiv ANH_2$)

1

interest in and use of this method have led us to investigate the chemical basis of the test.

The method was introduced by Emerson (2) in 1943; he suggested on the basis of analogy with other aromatic amines that the reaction led to the formation of a *p*-quinoneimide adduct (see Scheme 1).

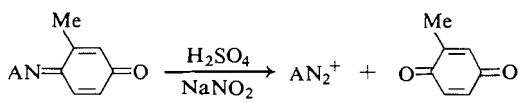
Para-coupling was proposed to explain the failure of the reaction with those phenols having



SCHEME 1

alkyl, aryl, nitroso, nitro, benzoyl, ester, and aldehyde groups in the para-position. However, certain *p*-substituted phenols did show a positive response and these groups (halo, carboxyl, alkoxyl, and sulfonic acid) were said to be expelled. No explanation of the nature of the "expulsion" was advanced.

Emerson and Sagal (3) later reported degradative evidence to support the proposed *p*-quinoneimide structure. *p*-Toluquinone was isolated following the hydrolysis, under diazotization conditions, of the dye obtained from *m*-cresol



SCHEME 2

Müller *et al.* (4) have since questioned the proposed expulsion of groups from the para-position. They were unable to detect the removal

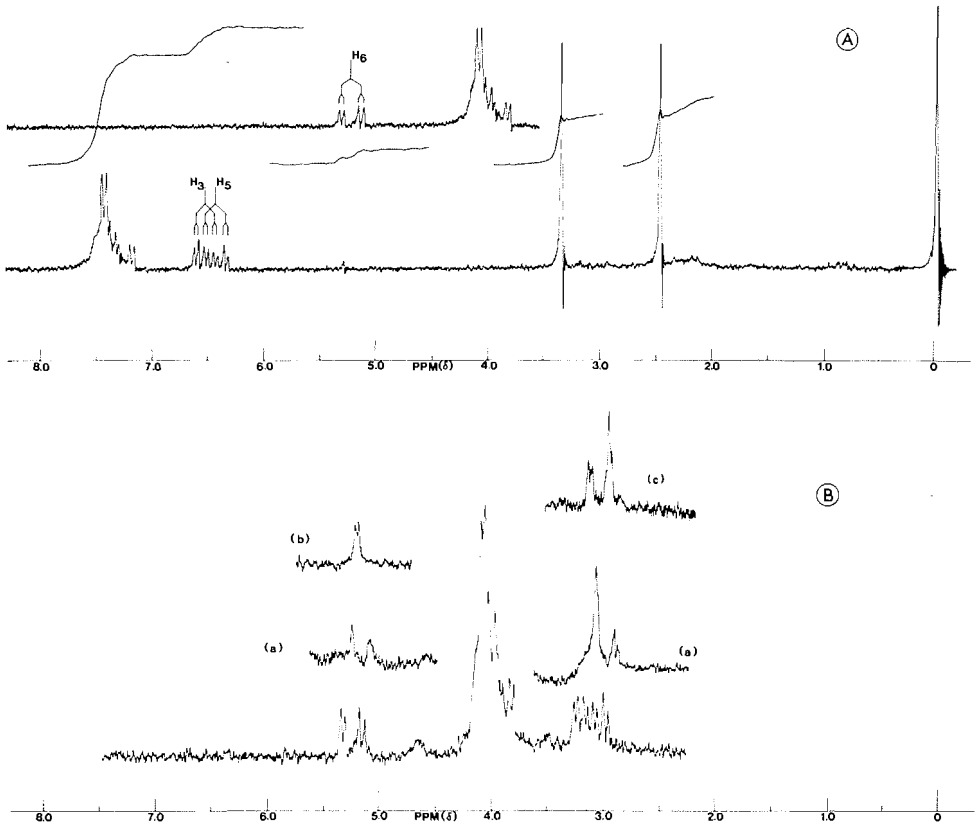


FIG. 1. (A) P.m.r. spectrum of phenol adduct, **2**. Upper trace offset 200 Hz. (B) Decoupled vinylic signals in **2**: (*a*) H_2 irradiated, (*b*) H_5 irradiated, (*c*) H_6 irradiated.

of carboxyl or alkoxyl substituents and consequently suggested that ortho-coupling had occurred. However, more recent studies (5–7) appear to confirm Emerson's original hypothesis. Dyes were isolated from the reactions of *p*-halophenols and the corresponding unsubstituted compounds. The products were found to be identical, confirming the elimination of the halogen atom. On the basis of visible spectra it was concluded that expulsion of *p*-alkoxyl and *p*-carboxyl groups also occurred. Elemental analyses on the isolated dyes gave empirical formulas corresponding to the structure of the expected *p*-quinoneimide adduct. Unfortunately, however, no other physical proof of structure was examined.

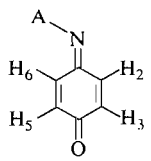
Thielemann (8) has recently shown that *p*-benzoquinone forms a dye with 4-AAP, which on chromatographic evidence is identical to that obtained from the oxidation of phenol. This might be taken as further proof of the *p*-quinoneimide structure. However, Okano and Uekama (9) reported that *p*-quinones gave colored products not only with 4-AAP, but also with other antipyrine derivatives where imide formation is impossible. They suggested that the formation of charge-transfer complexes was responsible for the color. Such complexes would, of course, also show the hydrolytic behavior quoted by Emerson as proof of the quinoneimide structure.

Thus there is no conclusive evidence for the structure of the dye products, and since such knowledge is essential for a fundamental understanding of the reaction pathway, we have consequently reinvestigated the Emerson reaction using modern spectroscopic techniques. The method chosen was to carry out the reaction with model phenols and to examine the p.m.r. spectra of the isolated dyes. As a result we have been able to assign the structure of the adducts unambiguously and further to reveal hitherto unobserved structural details.

Results and Discussion

Phenol and Reactive Para-substituted Phenols

Phenol and its *p*-chloro, -carboxyl, and -methoxy derivatives were found to react to each give a dye having a similar m.p. and an identical p.m.r. spectrum. This confirms the elimination of the latter two groups, previously proposed (6) on the basis of visible spectroscopy. The p.m.r. spectrum, shown in Fig. 1A, confirms the *p*-quinoneimide structure of the product **2**.



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Apart from the aromatic multiplet and the two methyl singlets arising from the antipyryl group, two vinylic multiplets can be seen. The doublet of doublets, which is at remarkably low field, is assigned (see later) to the proton H_6 which is *syn* to the antipyryl group and is coupled to both H_5 and H_2. The higher field signal, an eight line multiplet, must arise from the overlapping of the two doublets of doublets expected from the protons adjacent to the carbonyl group, H_3 and H_5. Integration of the spectrum suggested that the remaining signals due to H_2, the proton *anti* to the antipyryl group, are buried under the aromatic multiplet (in fact a portion of this signal appears to be visible).

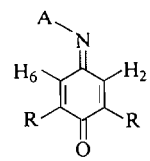
The position of H_2 was confirmed by spin-decoupling experiments, as shown in Fig. 1B. When the suspected H_2 region was irradiated, the signal due to H_6 collapsed to the expected doublet. Similarly the high field vinylic signal now appeared as a mixture of a doublet (one-half of the unchanged doublet of doublets due to H_5) and an unresolved multiplet (assumed to arise from superposition of the other half of the H_5 signal on the collapsed H_3 signal, predicted to be a doublet). A similar, but mirror image, situation was found in this region when H_6 was irradiated. Here H_5 is decoupled while H_3 is unchanged. Finally, the expected narrow doublet for H_6 was observed when H_5 was irradiated. These decoupling experiments reveal that the most deshielded of the protons adjacent to the imino group, H_6, is coupled to the most shielded of the protons adjacent to the carbonyl group, and the reverse. Thus, knowing the identity of H_6, it is possible to assign the identities of all the other ring protons.

The values observed for the vicinal coupling (J_{56}, $J_{23} \simeq 10$ Hz) and for the long-range cross-ring coupling (J_{26}, $J_{35} \simeq 2$ Hz) are of the magnitude reported for other quinone derivatives (10*a*). While the positions of the protons adjacent to the carbonyl group, H_3 and H_5, are very similar, those adjacent to the imino bond, H_2 and H_6, are separated by approximately 1.5 p.p.m., revealing that the antipyryl group has an extremely large anisotropic effect. A similar, but smaller, effect has been reported (11) in the spectra of quinonemonooximes and their anions.

The product from the reaction of *p*-benzoquinone with 4-AAP was identical to that obtained from the oxidation of phenol. Therefore the colors formed from *p*-quinones and 4-AAP are due to the formation of *p*-quinoneimides, and not to charge-transfer complexes, as previously suggested (9).

Symmetrical Ortho-disubstituted Phenols

Adducts **3** and **4** were obtained from 2,4,6-trichlorophenol and 2,6-dimethylphenol respectively. Their p.m.r. spectra are shown in Fig. 2.



3 R = Cl
4 R = Me

With the dichloro compound **3**, which provides a further example of the elimination of a *p*-chlorine atom, the low field doublet assigned to H_6, the proton *syn* to the antipyryl group, is the only visible vinylic signal. It is again assumed that the signal of the *anti* proton, H_2, is buried under the aromatic multiplet. Unfortunately, the low solubility of this compound prevented confirmation by accurate integration.

The p.m.r. spectrum of the dimethyl derivative **4** was unique among the compounds studied in that it revealed the signals of both the *syn* and *anti* proton. Both appeared as identical multiplets due to the additional long-range coupling with the allylic protons of the vicinal methyl group. This coupling, $J_{HCCMe} = 1.4$ Hz, of similar magnitude to those reported (10*b*) for analogous compounds, is also, as expected, shown in the six proton doublet due to these methyl groups.

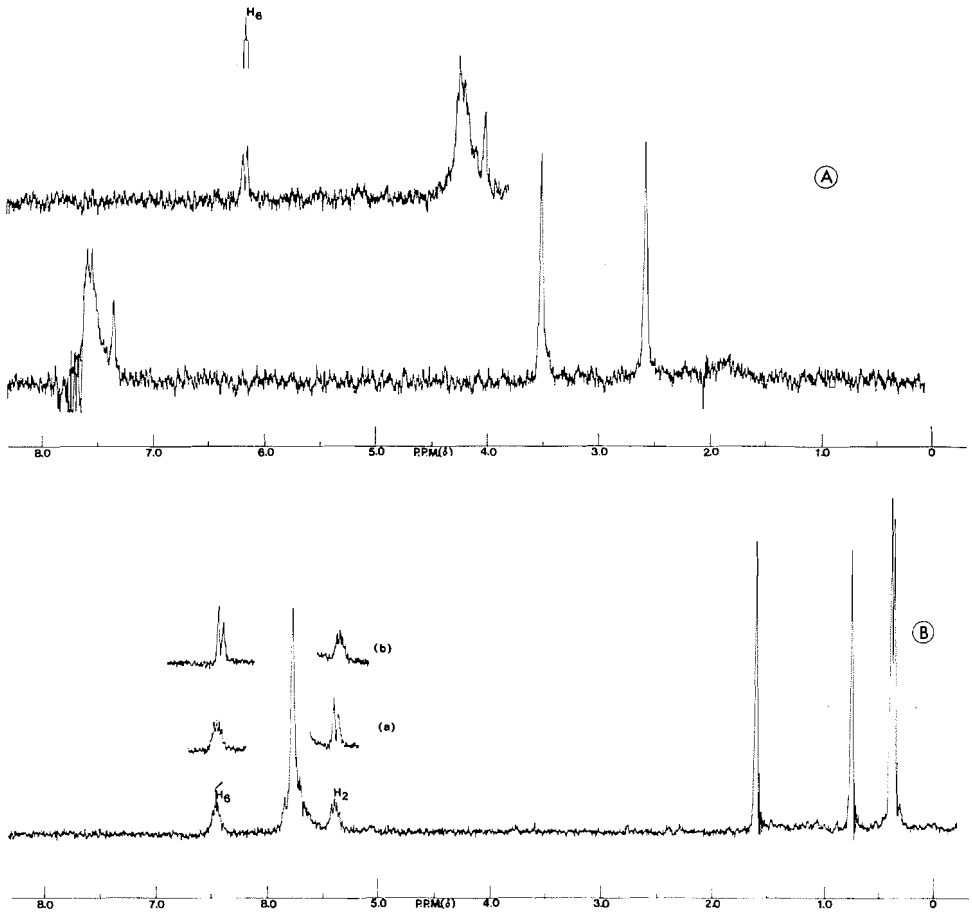


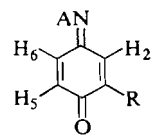
FIG. 2. (A) P.m.r. spectrum of 2,4,6-trichlorophenol adduct, **3**. Upper trace offset 200 Hz. (B) P.m.r. spectrum of 2,6-dimethylphenol adduct, **4**. Complete spectrum offset 100 Hz. Insert: (*a*) H_2 decoupled and (*b*) H_6 decoupled from vicinal methyl group.

When this doublet was irradiated and the H_2 and H_6 signals were examined, each was found to have collapsed to the expected doublet. Similarly, on irradiation of either H_2 or H_6 the methyl doublet collapsed to a broadened singlet.

The absence of signals in the δ 6.5 p.p.m. region in both compounds confirms the previous assignment of signals in this region of the phenol adduct **2** to the protons adjacent to the carbonyl group, H_3 and H_5.

Ortho-monosubstituted Phenols

The identical chloro compound **5** was obtained from both 2-chlorophenol and 2,4-dichlorophenol, confirming the report of Svobodova and Gasparic (6), while *o*-cresol gave the adduct **6**. Their p.m.r. spectra are shown in



5 R = Cl
6 R = Me

Fig. 3. Both compounds have a single proton H_5 adjacent to the carbonyl group and one might expect to find in each case a doublet for H_5, which is coupled only with H_6. However, both compounds show four lines in the appropriate region. This result suggests the formation of a mixture of *syn* and *anti* isomers in both cases, a doublet being obtained from each isomer. The presence of geometrical isomers is clearly shown in the appearance of the lowest field signals,

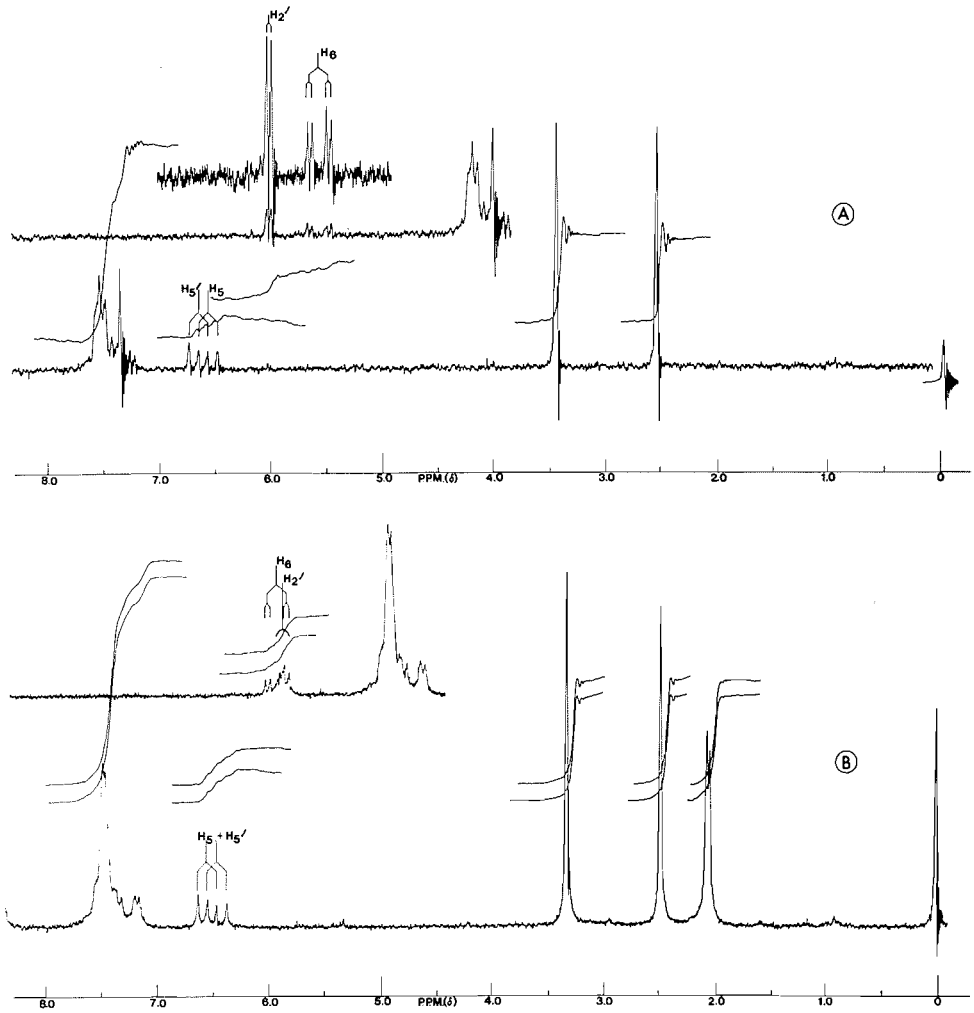
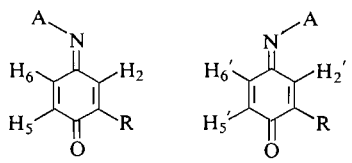


FIG. 3. (A) P.m.r. spectrum of 2-chlorophenol adducts, **5***a* and *b*. Upper trace offset 200 Hz. (B) P.m.r. spectrum of *o*-cresol adducts, **6***a* and *b*. Upper trace offset 150 Hz.



5 R = Cl
6 R = Me

which arise from a proton adjacent to the C=N bond and *syn* to the antipyryl group. Inspection of the chloro compounds, **5***a* and *b*, shows that these protons, H_6 and H_2', are not identical chemically. In the *anti* isomer **5***a* the proton H_6, coupled to both H_2 and H_5, should appear as a doublet of doublets, whereas in the *syn* isomer **5***b* this proton H_2' is only coupled to H_6' and should therefore be a doublet. Examination of Fig. 3A reveals the predicted splitting pattern. Spin-decoupling experiments confirm the proposed coupling assignments, and also reveal that in the four line high field vinylic signal due to H_5 and H_5', the former is the more shielded of the two protons. Again the protons adjacent to the C=N bond and *anti* to the antipyryl group, H_2 and H_6', appear to be hidden under the phenyl multiplet.

The lowest field signals of the *o*-cresol adducts, **6***a* and *b*, are more complex than those of the chloro analog, due to the additional long-range

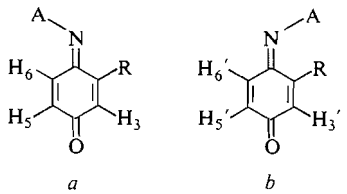
coupling of H_2' with the allylic protons of the vicinal methyl group. While one-half of the doublet of doublets due to H_6 is clearly visible, the other half is superimposed on the multiplet arising from H_2'. As with the chloro compounds the *anti* protons, H_2 and H_6', are not visible.

Comparison of the lowest field signals of **5** and **6** shows that in the chloro compound **5**, H_2' (adjacent to chlorine) is at lower field than H_6 (adjacent to hydrogen), while the reverse is true for the methyl analog **6**. Therefore the vinylic proton is deshielded by a vicinal chlorine atom and shielded by a vicinal methyl group. This follows the expected trend for substituted alkenes (10*c*).

In both cases approximately equal amounts of the *syn* and *anti* isomer appear to have been formed. This might have been anticipated, since there should be little interaction between the substituent and the remote antipyryl group, and consequently both isomers should be of similar energy.

Meta-monosubstituted Phenols

In all of the previous adducts **2**–**6**, the ring positions ortho to the C=N bond are unsubstituted. Although the signals of these protons, H_2 and H_6, are widely separated because of the anisotropy of the antipyryl group, it is not possible *a priori* to distinguish the identity of each signal. Accordingly the adducts **7** and **8** were prepared from 3-chlorophenol and *m*-cresol respectively. Here it might be anticipated



a *b*

7 R = Cl
8 R = Me

that unequal amounts of the *syn* and *anti* isomers would be produced, with the *anti* isomer *a* predominating in each case, because of unfavorable steric interaction between the substituent and antipyryl groups in the *syn* configuration. Examination of Fisher–Hirschfelder–Taylor models confirms that there is severe crowding in the *syn* isomer *b*.

The p.m.r. spectra illustrated in Fig. 4 clearly show in both cases a low field doublet. With the chloro compound **7**, integration of this doublet indicates that a single isomer, which from the above argument must be the *anti* isomer **7***a*, has been formed. Thus the lowest field signal must be due to H_6, the proton *syn* to the antipyryl group in the *anti* isomer. The presence of a single isomer appears to be confirmed by the high field vinylic signal, since only one doublet, due to coupling of H_3 with H_5, and one doublet of doublets, arising from the coupling of H_5 with both H_3 and H_6, are apparent.

A similar situation is found with the *m*-cresol adduct where again only a single isomer, **8***a*, appears to have been formed. The high field vinylic region is more complex than for the chloro compound due to additional long-range coupling of H_3 with the vicinal methyl group. The H_3 multiplet is superimposed upon one-half of the doublet of doublets due to H_5.

The formation of a single isomer, presumed to be *anti*, has also been noted (11) from the p.m.r. spectra of appropriately substituted quinone-oximes. The results allow us therefore to unambiguously assign signals for H_2 and H_6 in the previous compounds **2**–**6**.

The antipyryl group consequently can be seen to exert a substantial anisotropic effect, causing deshielding of a proton *syn* to it and adjacent to the C=N bond. While differences in the chemical shifts of *syn* and *anti* protons have been noted (10*d*) in the spectra of several classes of compounds having a C=N bond, the anisotropic effect of the antipyryl group is unusually large. The effect may be due to a conformation in which the *syn* proton may lie in the plane of the antipyryl carbonyl group and close to the oxygen atom, since large deshieldings have been noted (10*e*) in such cases. Examination of Fisher–Hirschfelder–Taylor models indicates that steric crowding may prevent free rotation of the antipyryl group around its external C—N bond and that in the resulting fixed conformation the *syn* hydrogen may in fact lie close to the antipyryl carbonyl oxygen.

In addition, the antipyryl group appears to have an opposite, but greatly reduced, effect on the *syn* proton meta to the C=N bond. Thus, in the phenol adduct **2** the *syn* proton H_5 is more shielded than the *anti* proton H_3. An identical result is found with the products from the ortho-substituted phenols **5** and **6**. In both cases, the *syn* proton H_5 in the *syn* isomer resonates at higher field than the corresponding *anti* proton H_5' of the *anti* isomer.

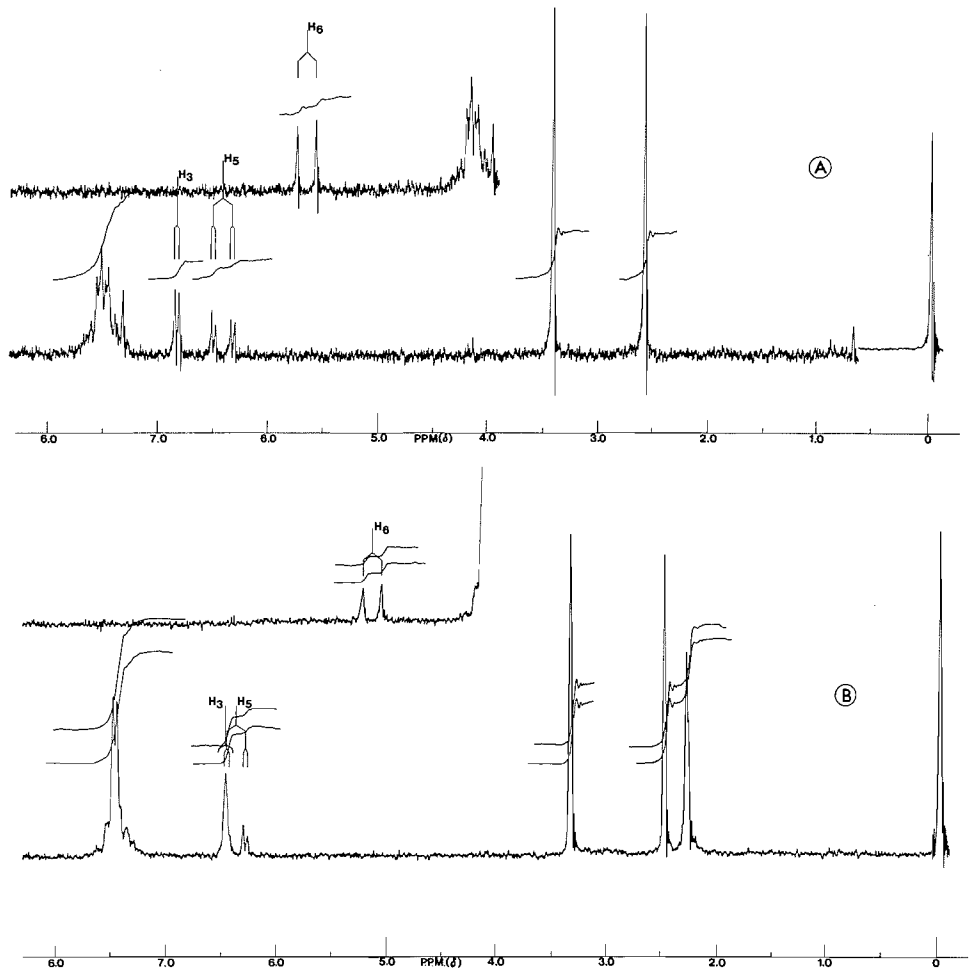


FIG. 4. (A) P.m.r. spectrum of 3-chlorophenol adduct, **7***a*. Upper trace offset 200 Hz. (B) P.m.r. spectrum of *m*-cresol adduct, **8***a*. Upper trace offset 200 Hz.

Experimental

P.m.r. spectra were recorded on a Varian A-60 spectrometer in deuterochloroform solvent and with tetramethylsilane as an internal standard. Spin-decoupling experiments were carried out using a Model V-6058 spin-decoupler.

Buffer solutions of p*H* 10.4 and 6.86 were prepared by dissolving dry buffer salt (Fisher) in distilled water. Buffer solutions for the p*H* 8 region were prepared by adjusting the latter, using a p*H* meter, to the appropriate p*H* by addition of dilute ammonia. 4-Aminoantipyrine (Aldrich) and the starting phenols were purchased from commercial suppliers and were used without further purification.

Melting points were taken on a hot stage apparatus and are uncorrected. Microanalyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee.

Preparation of Dyes

To a stirred mixture of 1 mmol of the given phenol and 0.35 g (1.5 mmol) of 4-aminoantipyrine in 75 ml of the appropriate buffer solution was added 2.7 g (10 mmol) of potassium persulfate dissolved in 50 ml of the same buffer solution. On mixing, a red color formed instantaneously and precipitation commenced rapidly. The reaction mixture was stirred for 30–60 min and the precipitate was then filtered off and washed several times with distilled water. The solid was then dried in air.

The yield and m.p. of purified samples are recorded in Table 1. P.m.r. spectral data are reported in Tables 2 and 3 (see text for interpretation). In those cases where formation of geometrical isomers was possible, comparison with the p.m.r. spectrum of the crude product indicated that recrystallization had not markedly effected the isomer ratio.

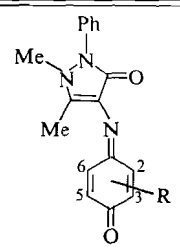
With potassium persulfate as oxidizing agent, only in the case of 2- and 3-chlorophenol was there any indication of the formation of significant amounts of any side-product(s). The unidentified side-product(s) showed several peaks in the δ 2.0–3.5 p.p.m. region. In the case of 3-chlorophenol it was not possible to obtain

TABLE 1. Preparation of *p*-quinoneimide dyes

Starting phenol	Product	p*H*	Yield (%)	M.p. (°C)
Phenol	**2**	10.4	69	165–168[a,e]
4-Hydroxybenzoic acid	**2**	10.4	68	163–167[b,e]
4-Chlorophenol	**2**	8.1	76	163–167[a,e]
4-Methoxyphenol	**2**	8.2	25	165–169[c,e]
2,4,6-Trichlorophenol	**3**	8.1	55	182–184[d,f]
2,6-Dimethylphenol	**4**	8.8	57	168–174[d,g]
2,4-Dichlorophenol	**5**	8.1	68	168–171[b,h]
2-Chlorophenol	**5**	10.4	56	162–167[b,h]
o-Cresol	**6**	8.0	72	159–164[c,i]
3-Chlorophenol	**7**	10.4	43	169–172[b,j]
m-Cresol	**8**	8.2	75	164–168[a,k]

[a]Recrystallized from dichloromethane – 100–120° petroleum ether.
[b]Recrystallized from chloroform – 100–120° petroleum ether.
[c]Recrystallized from benzene.
[d]Recrystallized from benzene – 100–120° petroleum ether.
[e]Literature (6) m.p. 168–170°.
[f]Anal. Calcd. for $C_{17}H_{13}Cl_2N_3O_2$: C, 56.37; H, 3.62; N, 11.60. Found: C, 56.59; H, 3.64; N, 11.45.
[g]Anal. Calcd. for $C_{19}H_{19}N_3O_2$: C, 71.01; H, 5.96; N, 13.08. Found: C, 71.23; H, 6.04; N, 12.94.
[h]Literature (6) m.p. 172–174°.
[i]Literature (5) m.p. 162–165°.
[j]Literature (7) m.p. 179–183°.
[k]Anal. Calcd. for $C_{18}H_{17}N_3O_2$: C, 70.34; H, 5.58; N, 13.67. Found: C, 70.34; H, 5.50; N, 13.04.

TABLE 2. Chemical shift data for *p*-quinoneimide adducts[a]



Compound	H_2	H_3	H_5	H_6	Ph	NMe	CMe	Other
2	Buried under phenyl	6.54 (d of d)	6.45 (d of d)	8.51 (d of d)	7.2–7.7 (m)	3.35 (s)	2.49 (s)	—
3 ($R_3 = R_5 = Cl$)	Buried under phenyl	—	—	9.52 (d)	7.3–7.7 (m)	3.51 (s)	2.59 (s)	—
4 ($R_3 = R_5 = Me$)	7.08 (m)	—	—	8.13 (m)	7.2–7.6 (m)	3.25 (s)	2.43 (s)	2.02 (d)(3,5-diMe)
5[b] ($R_3 = Cl$)	Buried under phenyl (H_2)	—	6.60 (d)(H_5)	8.94 (d of d) (H_6)	7.2–7.8 (m)	3.47 (s)	2.55 (s)	—
	9.42 (d)(H_2')		6.69 (d)(H_5')	Buried under phenyl (H_6')				
6[b] ($R_3 = Me$)	Buried under phenyl (H_2)	—	6.45 (d)(H_5)	8.48 (d of d)(H_6)	7.1–7.8 (m)	3.30 (s)	2.45 (s)	2.05 (d)(3-Me)
	8.41 (m)(H_2')		6.52 (d)(H_5')	Buried under phenyl (H_6')				
7 ($R_2 = Cl$)	—	6.85 (d)	6.44 (d of d)	9.03 (d)	7.2–7.8 (m)	3.42 (s)	2.60 (s)	—
8 ($R_2 = Me$)	—	6.49 (m)	6.39 (d of d)	8.51 (d)	7.2–7.7 (m)	3.34 (s)	2.49 (s)	2.28 (d)(2-Me)

[a]Chemical shifts are given as δ values followed by the multiplicity (m = multiplet, s = singlet, d = doublet, d of d = doublet of doublets).
[b]Mixture of *syn* and *anti* isomers. Primed values are those for the *anti* isomer (see text).

TABLE 3. Spin–spin coupling constants (Hz) of *p*-quinoneimide adducts assuming first-order splitting

Compound	
2	$J_{26} = 2.5, J_{35} = 2.1, J_{23} = 10.5, J_{56} = 10.3$
3	$J_{26} \simeq 2$
4	$J_{26} = 2.5, J_{HCCMe} = 1.4$
5	$J_{26} = J_{2'6'} = 2.6, J_{56} = 10.4, J_{5'6'} = 10.0$
6	$J_{26} = 2.8, J_{56} = 10.4, J_{5'6'} = 10.1$
7	$J_{35} = 2.4, J_{56} = 10.3$
8	$J_{35} = 2.4, J_{56} = 10.2, J_{HCCMe} = 1.2$

a pure sample of **7** by recrystallization, although the p.m.r. spectrum showed that it was present and only in the *anti* form **7***a*. This difficulty was overcome by the substitution of 6.6 g (20 mmol) of potassium ferricyanide as oxidizing agent. In this case there was no impurity formation and **7***a* was the sole product. Similar difficulties with these and other halophenols have been noted (7).

Reaction Between p-Benzoquinone and 4-Aminoantipyrine

Addition of 0.108 g (1 mmol) of *p*-benzoquinone (yellow) and 0.203 g (1 mmol) of 4-aminoantipyrine (cream) to 10 ml of chloroform gave a red solution. This was allowed to stand in the dark for 70 h. Addition of 100–120° petroleum ether caused the precipitation of a reddish brown solid. This was filtered off to give 0.262 g (89%) of **2**, m.p. 162–167°. Recrystallization from benzene – 100–120° petroleum ether gave 0.215 g (73%) of red crystals, m.p 166–169°. The p.m.r. spectrum of the product was identical to that of the compound from the oxidation of phenol.

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