The Synthesis and Oxidation of 4-(*N*-Arylmethylideneamino)-2,6-di-*t*-butylphenols

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4-(*N*-Arylmethylideneamino)-2,6-di-*t*-butylphenols (I) were synthesized through the condensation of 4-amino-2,6-di-*t*-butylphenol hydrochloride and arylaldehydes, and the infrared and electronic spectra of phenols (I) were discussed. The oxidation of phenol (I) with lead dioxide gave a stable phenoxyl radical (II) in solution, and 4,4′-bis[4-(*N*-arylmethylideneamino)-2,6-di-*t*-butyl-2,5-cyclohexadien-1-one] (III) was isolated as a crystalline oxadation product, which was in equilibrium with the radical (II) in solution.

A number of stable 2,6-di-*t*-butylphenoxyl radicals are known to be derived from 2,6-di-*t*-butylphenol derivatives.[1,2] As for 2,6-di-*t*-butylphenoxyl radicals with a double bond at the 4-position of the phenoxyl ring, a few reports have been published on derivatives with –CH=CH–Ar,[3,4] –N=N–Ar,[5] and –CH=N–Ar[6] groups. The synthesis, properties and oxidation of 4-(*N*-arylmethylideneamino)-2,6-di-*t*-butylphenol (I), which is a novel Schiff base in 2,6-di-*t*-butylphenol derivatives, were studied, and the results will be reported in this paper.

Results and Discussion

Schiff bases are generally synthesized through the condensation of amines and aldehydes in ethanol at room temperature,[7] and the maximum yield is attained at the pH range of the reaction mixture of 6—8.[8] Thus, phenols (I) have been prepared through the condensation of arylaldehydes and 4-amino-2,6-di-*t*-butylphenol hydrochloride in the presence of pyridine, since the free aminophenol is quite an unstable compound. Condensation proceeded very easily, and crystals of phenols (I) precipitated from the reaction mixture in a few minutes. The yields of phenols (I) are given in Table 1. Considerable amounts of red-brown, tarry compounds were obtained as by-products, and they might have originated from the oxidation of 4-amino-2,6-di-*t*-butylphenol hydrochloride. In the absence of pyridine, a methoxy derivative of phenol (I) (19%) was obtained after letting the reaction mixture stand for one hour at room temperature, but no other phenols (I) were obtained even after a long period of condensation. This was caused by a decrease in the pH value of the reaction mixture.

Table 1. Syntheses of phenol (I)

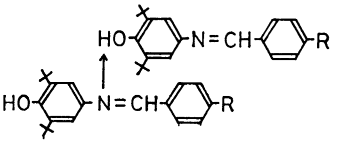
R	Aryl-aldehyde (mol/EtOH, ml)	4-Amino-2,6-di-*t*-butyl-phenol·HCl (mol/EtOH, ml)	Pyridine (mol)	Reaction time (hr)	Yield (%)
NO_2	0.021/30	0.021/ 5	0.021	1	50
			—	24	—
COOMe	0.012/20	0.012/ 3	0.012	1	53
			—	24	—
Cl	0.021/ 7	0.021/ 5	0.021	1	61
			—	24	—
Unsubst.	0.021/—	0.021/15	0.021	1	43
			—	24	—
MeO	0.021/—	0.021/10	0.021	1	38
			—	1	19

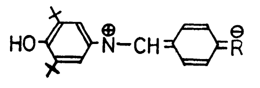
Table 2. Infrared spectra of phenol (I)

R	ν_{OH} (cm^{-1}) free	ν_{OH} (cm^{-1}) assoc.	$\nu_{C=N}$ (cm^{-1})	Medium
NO_2	3630m	3430m	1620w	KBr
	3630s	—	1625w	CCl_4
COOMe	3630m	3410m	1620m	KBr
	3630s	—	1625m	CCl_4
Cl	3630m	3400w	1620m	KBr
	3630s	—	1625m	CCl_4
Unsubst.	3630vw	3150m	1610m	KBr
	3630s	—	1625m	CCl_4
MeO	3630vw	3230m	1615m	KBr
	3630s	—	1625m	CCl_4

ν, stretching; s, strong; m, medium; w, weak; vw, very weak

The infrared spectra of a carbon tetrachloride solution and a KBr disk of phenol (I) were measured, and the results are given in Table 2. The characteristic ν_{OH} bands were observed at 3630—3150 cm^{-1}, and the $\nu_{C=N}$ bands at 1625—1610 cm^{-1}. The strong band of a free OH group was observed at 3630 cm^{-1} for the carbon tetrachloride solution of each phenol (I). In the solid state, however, the intensity of these bands changed to medium for nitro, methoxycarbonyl and chloro derivatives, and to very weak for unsubstituted and methoxy derivative of phenol (I). Correspondingly, broad bands of associating OH groups appeared at 3410—3150 cm^{-1} for phenols (I), and the intensity of the bands of the unsubstituted and methoxy derivative was stronger than the others. The location of $\nu_{C=N}$ bands tended to shift to lower wave numbers in the solid state than in solution. These observations suggest that, in the solid state, phenols (I) are associating as shown below and the bond orders of OH and C=N bonding become lower than in solution. The location of $\nu_{C=N}$ bands of phenols (I) in solution was almost constantly at 1625 cm^{-1}, and no substituent effect was





(I')

observed. This can be explained by the minor participation of a resonance structure (I′) since the electron-attracting power of the sp^2 nitrogen atom compensates that of an electron-attracting substituent. The location of ν_{OH} bands of phenols (I) in solution was at 3630 cm^{-1} and was also independent of the substituents. This may be due to the above resonance effect and to the twisting of the bonding between a nitrogen atom and a phenol ring.[9]

TABLE 3. ELECTRONIC SPECTRA OF PHENOL (I) IN *n*-HEXANE

R	λ_{max}, nm ($\varepsilon \times 10^{-4}$)		
NO_2	262.5(1.73)	303(0.85)	383(1.58)
COOMe	260 (2.02)	282(1.39)	360(1.43)
Cl	253.5(1.83)	274(1.43)	347(1.29)
Unsubst.	252.5(1.04)	271(1.09)	342(1.06)
MeO	251.5(1.04)	281(2.06)	338(1.54)

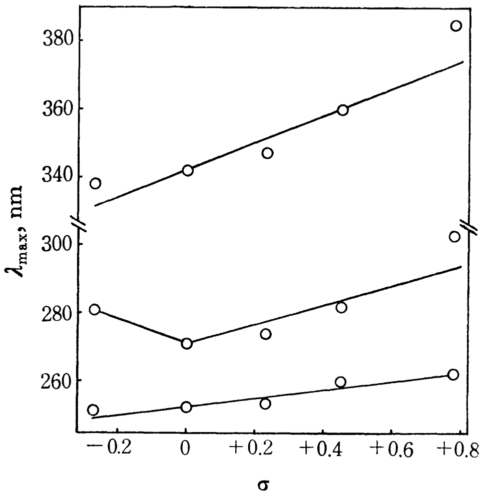


Fig. 1. The correlation of Hammett substitution constants with the wavelength of the absorption maxima of phenols (I)

The electronic spectra of phenols (I) in *n*-hexane were measured and the results are shown in Table 3. Each derivative of phenols (I) has three absorption bands near at 350, 290, and 250 nm, and these bands are similar to those of benzalanilines.[10] Figure 1 gives the correlation of the Hammett substituents (σ)[11] and the wavelength of each absorption maximum. A simple bathochromic effect of the electron-attracting group is observed in the absorption bands at 250 and 350 nm, whereas the same effect is caused by both electron-attracting and electron-releasing group in the bands at 280 nm. These bands may be assigned to result from a charge transfer from the phenol ring to the –N=CH– bonding, from electronic transition throughout the whole π-electron system, and from local excitation without charge transfer.[10]

Phenols (I) in tetrahydrofuran were oxidized with excess amounts of lead dioxide at room temperature under nitrogen atmosphere. The color of each reaction mixture turned from yellow to red-brown or yellow-green. The ESR measurement of the reaction mixture of each phenol (I) showed the presence of a stable radical, and the spectrum was considered to be made up of a triplet (with an equal intensity) of triplet (with intensity ratio of 1: 2: 1) (Fig. 2). The observed ESR signals may be assigned to the phenoxyl radical (II), since an odd electron on a nitrogen atom gave a triplet signal (with an equal intensity), and then each peak of this triplet was further split to a triplet (with intensity ratio of 1: 2: 1) by two equivalent *m*-ring protons. The observed ESR hyperfine splitting (Hfs) constants of the radicals (II) are given in Table 4.

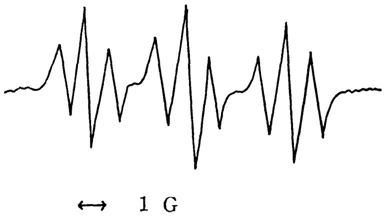
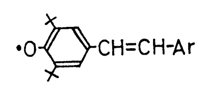


Fig. 2. ESR spectrum of radical (II, R=NO_2)

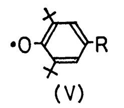
TABLE 4. ESR COUPLING CONSTANTS OF RADICALS (II)

R	a_{m-H} (gauss)	a_N
NO_2	1.1	3.4
COOMe	1.2	4.2
Cl	1.0	3.9
Unsubst.	1.0	3.8
MeO	1.1	4.8

The small Hfs value of the nitrogen atom is due to the small spin density on the nitrogen atom, which may be caused by the twisting of the bonding between the nitrogen atom and the phenol ring.[9] The absence of hyperfine splitting by a proton of the methine group may be due to the very small spin density on the methine group. This suggests the very small participation of allylic resonance in the radical (II) which was reported with radical (IV).[3] The Hfs value of the *m*-ring proton is independent of the substituents in the radical (II), though a substituent effect was reported with phenoxyl radicals (V).[12] This may be explained by a non-planarity which has been previously been described and by the remoteness of the substituents from the *m*-ring protons.



(IV)



(V)

Yellow crystalline oxidation products were isolated from the reaction mixture of nitro, methoxycarbonyl and chloro derivatives of phenol (I), but unsubstituted and methoxy derivatives gave a tarry material. These crystalline oxidation products of the above three phenol derivatives were not so stable at room temperature and decomposed at their melting points. The results of the isolated crystalline oxidation products are shown in Tables 5 and 6. The results of the elementary analyses

Table 5. Synthesis of cyclohexadienone (III)

R	React. time (min)	Yield (%)	Mp (°C)	Anal. (%) Found (Calcd) C	H	N	Cl	MW. Found VPO	MS	Calcd
N_2O	45	24	152—154	70.69	7.07	7.69	—	692	777	706.9
				(71.36	7.13	7.93	—)			
COOMe	60	16	162—164	74.93	7.73	3.66	—	554	788	732.9
				(75.38	7.70	3.82	—)			
Cl	30	15	119—121	73.10	7.36	4.01	10.52	559	766	685.7
				(73.56	7.35	4.09	10.34)			

Table 6. Spectral data of cyclohexadienone (III)

R	Infrared spectra cm^{-1}, KBr	Electronic spectra λ_{max} nm, ($\varepsilon \times 10^{-4}$)
NO_2	3030, 2950(ν_{CH}), 1650 ($\nu_{C=O}$), 1630 ($\nu_{C=C}$), 1620sh ($\nu_{C=N}$), 1605 (phenyl), 1520, 1345 (ν_{NO_2}), 1245 (*t*-butyl), 820 (δ_{CH})	286 (6.8) 403 (0.2)
COOMe	3030, 2950 (ν_{CH}), 1720, 1650 ($\nu_{C=O}$), 1630 ($\nu_{C=C}$), 1620sh ($\nu_{C=N}$), 1600 (phenyl), 1275 (ν_{C-O}), 1250 (*t*-butyl), 1115 (ν_{C-O}), 820 (δ_{CH})	285 (5.4) 395 (0.8)
Cl	3030, 2950 (ν_{CH}), 1650 ($\nu_{C=O}$), 1630 ($\nu_{C=C}$), 1620sh ($_{C=N}$), 1595 (phenyl), 1245 (*t*-butyl), 820 (δ_{CH})	285 (4.1) 397 (0.6)

ν, stretching; δ, bending; sh, shoulder. Electronic spectra were taken for cyclohexane solution of 2.0×10^{-5} M.

(Table 5) were in good agreement with the calculated values for a dimer of the radical (II). The absence of the ν_{OH} band (3630 cm^{-1}) and the appearance of the $\nu_{C=O}$ band (1650 cm^{-1}) and the $\nu_{C=C}$ band (1630 cm^{-1}) in their infrared spectra (Table 6) suggest that these oxidation products have the 2,5-cyclohexadienone structure.[13] The chemical structure of the dimer of the radical (II) depends on the way of the recombination reaction of the radical (II), *e.g.*, oxygen-carbon coupling, *etc.* The most probable recombination reaction is coupling at the 4-carbon atom of the phenol ring, since oxygen-oxygen coupling is not known with 2,6-di-*t*-butylphenoxyl radicals,[1,2] and since the spin density at the 4-carbon atom is known to be relatively high,[2] whereas ESR measurement showed quite a low spin density on the methine group of the radical (II). Therefore, each isolated oxidation product is 4,4′-bis-[4-(*N*-arylmethylideneamino)-2,6-di-*t*-butyl-2,5-cyclohexadien-1-one] (III). The mass spectrum of each oxidation product showed not only a weak molecular ion peak of cyclohexadienone (III), but also a weak peak of a larger mass number than the above molecular ion peak (Table 5). These unexpected peaks might arise from the formation of some compound in the ion-chamber of a mass spectrometer through the thermolysis and recombination of samples. The mass number of these peaks suggests that the molecular formula of the generating compound is $C_{43}H_{61}N_2O_3Ar$ ($Ar=C_6H_4NO_2$, $C_6H_4COOCH_3$, and C_6H_4Cl, respectively), since the difference in the unexpected mass number of each sample was equal to that in the molecular weight of the corresponding substituents, thus indicating the existence of one aryl group in each generating compound. The molecular weight measurement of oxidation products in benzene by a vapor pressure osmometer gave smaller values than the values calculated for cyclohexadienone (III) (Table 5). The sample solution for molecular weight measurement showed the same ESR spectra as those observed in the

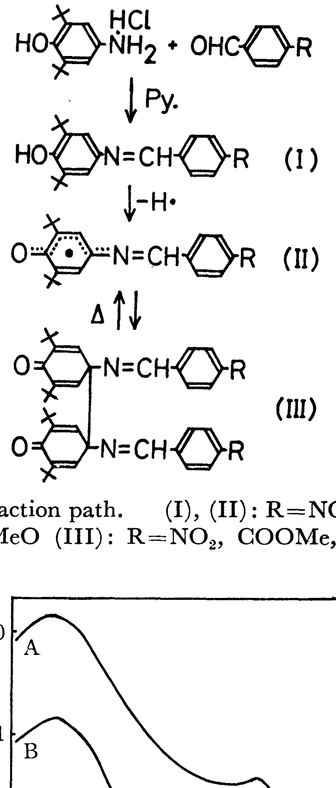


Fig. 3. Reaction path. (I), (II): $R=NO_2$, COOMe, Cl, H, MeO (III): $R=NO_2$, COOMe, Cl

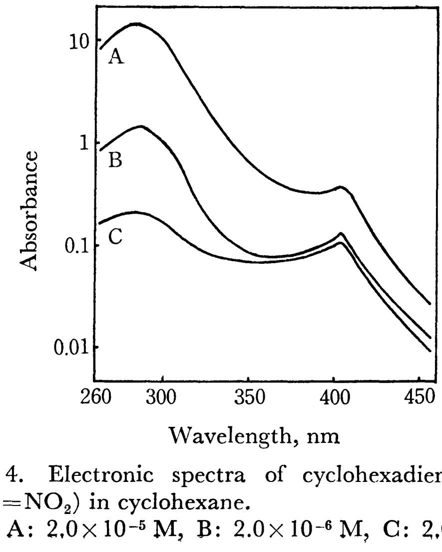


Fig. 4. Electronic spectra of cyclohexadienone (III, $R=NO_2$) in cyclohexane.
A: 2.0×10^{-5} M, B: 2.0×10^{-6} M, C: 2.0×10^{-7} M

oxidation of phenols (I). The intensity of these ESR signals increased with the rise of temperature, and *vice versa*, and the ESR signals faded gradually at high temperature. These results show the dissociation of cyclohexadienones (III) to radicals (II) in solution, and those radicals then decompose to some other compounds at high temperature. The color of a benzene solution of cyclohexadienone (III) changed from yellow to green with the rise of temperature and returned to yellow upon a lowering of temperature. This color changing can be explained by the above dissociation. The electronic spectra of cyclohexadienones (III) at room temperature showed strong absorption bands near 285 nm and very weak bands near 400 nm (Table 6). The latter bands are due to radicals (II), since the dilution of the sample solution increased the relative intensity of these bands (Fig. 4).

Experimental

*4-Amino-2,6-di-*t*-butylphenol Hydrochloride.* 4-Nitroso-2,6-di-*t*-butylphenol[14] (14.1 g, 0.06 mol) and zinc powder (9.8 g, 0.15 mol) were suspended in methanol (180 ml). Hydrochloric acid (35 ml, *ca.* 0.35 mol) was added drop by drop to this suspension over 45 min under refluxing, which was then continued for 30 min after the addition of hydrochloric acid. Then the excess zinc powder was filtered from the reaction mixture, and the solvent (*ca.* 140 ml) was distilled from the filtrate. The concentrate was poured onto cold, degassed water, and the precipitating product was filtered and washed with cold, degassed water and then with cold *n*-hexane. The above isolating process was carried out under a nitrogen atmosphere. The subsequent drying of the product under reduced pressure gave a white powder of crude 4-amino-2,6-di-*t*-butylphenol hydrochloride (13.0 g, 84%, mp 195—203 °C (dec.) (lit,[15] 201—204 °C)), which was used for the preparation of phenols (I) without further purification.

*4-(*N*-Arylmethylideneamino)-2,6-di-*t*-butylphenols (I).* Arylaldehyde in ethanol and pyridine were added to an ethanol solution of 4-amino-2,6-di-*t*-butylphenol hydrochloride, after which the reaction mixture was allowed to stand for 1 hr at room temperature. The precipitating phenol (I) was filtered and washed successively with cold methanol, water and *n*-hexane. Each crude powder of phenol (I) was recrystallized from *n*-hexane. The follwing melting points were observed for each crystal of phenol (I): R=NO_2: yellow-orange needles, 169.0—170.0 °C; R=COOMe: yellow needles, 158.0—160.0 °C; R=Cl: pale yellow needles, 144.0—145.0 °C; Unsubstituted: yellow-orange needles, 151.0—152.0 °C; R=MeO: pale yellow plates, 155.0—157.0 °C. The results of elementary analyses and the molecular weight determination (MS) for prepared phenols (I) were in good agreement with the calculated values.

*4,4′-Bis[4-(*N*-arylmethylideneamino)-2,6-di-*t*-butyl-2,5-cyclohexadien-1-one] (III).* Phenol (I) (2×10^{-4} mol) in dried tetrahydrofuran (20 ml) was put in a Schlenk tube, and lead dioxide (0.09 g, 4×10^{-4} mol) was added to this solution. The reaction mixture was degassed by freezing with liquid nitrogen and brought to room temperature under a nitrogen atmosphere. Oxidation was carried out by shaking the reaction mixture at room temperature for the period shown in Table 5. Then lead oxide was filtered off from the reaction mixture, and the filtrate was evaporated to dryness under reduced pressure. The residual compound was dissolved in degassed cyclohexane (*n*-hexane for the chloro derivative) at room temperature, and the subsequent suitable concentration of this solution under reduced pressure gave yellow crystalline cyclohexadienone (III).

All the melting points were uncorrected. The molecular weight of cyclohexadienone (III) was determined for a benzene solution (0.007 M) at 37 °C with a Mechrolab 302 vapor pressure osmometer. The infrared spectra were recorded with a Shimadzu IR-27G grating spectrophotometer, the electronic spectra, with a Hitachi EPS-2U recording spectrometer, and the ESR spectra, with a Hitachi 771 electron spin resonance spectrometer equipped with a variable temperature accessory.

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