Ferricyanide Oxidation of 4-Arylazo-2,6-di-*t*-butylphenols

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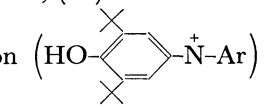
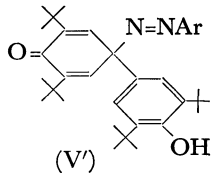
Alkaline ferricyanide oxidation of 4-arylazo-2,6-di-*t*-butylphenols (I) gave molecular nitrogen, diphenyl derivatives (VI), 2,6-di-*t*-butyl-*p*-benzoquinone-*N*-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)arylhydrazone (V) and red tarry compounds. Picryl derivative of phenol (I) gave 2,6-di-*t*-butyl-*p*-benzoquinone-picrylanil (X) instead of hydrazone (V). The reaction path was studied on the basis of isolated compounds.

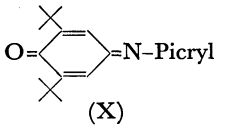
4-Arylazo-2,6-di-*t*-butylphenols (I) have been found to give some mixtures of stable free radicals by alkaline ferricyanide oxidation.[1] The oxidation products of phenols (I: Ar=*p*-nitrophenyl, *p*-chlorophenyl, phenyl, *p*-methoxyphenyl, and picryl) and the reaction path were studied, and the results are reported in this paper. A few papers have appeared on the oxidation of hydroxyazo dyes as studied by the synthesis of azoxy compounds, photochemical or oxidative color fading,[2,3] and the effect of chemical structure on reactivity.[4-7] Azoxy compounds, phthalic acid and some phenolic compounds were obtained by hydrogen peroxide oxidation,[2] and quinone derivatives and other compounds were obtained by oxidation with ceric sulphate,[3] lead peroxide,[4] ferric chloride,[5] sodium hypochlorite,[7] and molecular oxygen.[6] These oxidation reactions were carried out under acidic conditions and little is known about the reaction path.

Results and Discussion

Benzene solution of phenols (I: Ar=*p*-nitrophenyl, *p*-chlorophenyl, phenyl, *p*-methoxyphenyl, and picryl), prepared from 2,6-di-*t*-butyl-*p*-benzoquinone and aryl hydrazine hydrochlorides, were oxidized with an aqueous solution of potassium ferricyanide and potassium hydroxide accompanied by vigorous evolution of molecular nitrogen. The reaction was stopped in a few minutes at the end of vigorous gas evolution, though slight gas evolution was observed to continue for a few hours. Picryl derivative of phenol (I: Ar=picryl), which has strong electron-attracting groups and exists completely as a hydrazone tautomer,[8] showed quite slow gas evolution and required a longer period of oxidation than the other four phenols (I). After the organic layer of the reaction mixture was left standing until stable free radicals in it had almost faded away, tarry residual compounds were obtained by distilling off the solvent. Appropriate purification of the residual compounds gave 2,6-di-*t*-butyl-*p*-benzoquinone-*N*-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)arylhydrazones (V: Ar=*p*-nitrophenyl, *p*-chlorophenyl, phenyl, and *p*-methoxyphenyl), diphenyl derivatives (VI: Ar=*p*-nitrophenyl, *p*-chlorophenyl, phenyl, *p*-methoxyphenyl, and picryl), 2,6-di-*t*-butyl-*p*-benzoquinone (VIII), 3,3′,5,5′-tetra-*t*-butyldiphenoquinone (IX), 2,6-di-*t*-butyl-*p*-benzoquinonepicrylanil (X) and a large amount of red brown tarry compounds. The chemical structures of these oxidation products were determined by means of their melting points, elemental analyses, infrared spectra, and mass spectra. The presence of ν_{OH} band at 3630 cm^{-1}, the value of the molecular ion peak (M^+) and elemental analyses offered two isomeric forms (V) and (V′) for hydrazones (V). However, (V′) was excluded since the peak of a fragment ion  was observed in the mass spectra, but the characteristic strong absorption bands (1670 and 1630 cm^{-1}) of 4-substituted-2,5-cyclohexadienone[9,10] were not observed in the infrared spectra.



(V′)



(X)

One of the oxidation products of picryl derivative of phenol (I: Ar=picryl) was found to be an anil derivative (X) from its mass spectrum (M^+), infrared spectrum (absence of ν_{OH} band) and elemental analysis. Diphenyl derivatives (VI) were isolated from the oxidation products of each phenol (I). A very small amount of 3,3′,5,5′-tetra-*t*-butyldiphenoquinone (IX) was isolated from the oxidation products of nitro derivative of phenol (I: Ar=*p*-nitrophenyl), and a trace amount of 2,6-di-*t*-butyl-*p*-benzoquinone (VIII) was detected in the oxidation products of unsubstituted derivative of phenol (I: Ar=phenyl). Their melting points were the same as those in literature and their infrared spectra were consistent with the structures. The rest of the oxidation products were tarry materials which could not be crystallized, and were found to be of phenolic character from the infrared spectra. The yields of oxidation products are given in Table 1. The yields of hydrazones (V) and diphenyl derivatives (VI) are not high. Substituent effect on the yield seems apparent. This might be caused by the difficulty of isolating these compounds. High yields of diphenyl derivative (VI) and molecular nitrogen, and low yields of hydrazone (V) were ob-

1) E. Manda, This Bulletin, **41**, 1743 (1968).
2) D. Haller and G. Ziersch, *Melliand textilber.*, **10**, 951 (1923).
3) A. N. Desai and C. H. Giles, *J. Soc. Dyers. Colourists.*, **65**, 639 (1949).
4) R. Willstäter and M. Benz, *Ber.*, **39**, 3482 (1906).
5) O. N. Witt and J. Dedichen, *ibid.*, **30**, 2655 (1897).
6) T. Zincke and P. Wiegand, *Ann.*, **286**, 85 (1895).
7) A. Seyewetz and E. Chaix, *Bull. Soc. Chim. Fr.*, **41**, 332 (1927).
8) E. Manda, This Bulletin, **44**, 1620 (1971).
9) E. Müller and K. Ley, *Chem. Ber.*, **87**, 922 (1954).
10) N. P. Neureiter, *J. Org. Chem.*, **28**, 3486 (1963).

Table 1. Oxidation products of phenols (I)

Ar of (I)	Oxidizing agent (mole ratio)	Reaction time (min)	Yields of oxidation products (%) (V)	(VI)	Other compound	N_2
p-Nitrophenyl	1.1	7	27.2	15.0	trace of IX	40.8
	5.0	30	18.0	33.0	trace of IX	59.2
	7.5	420	—	24.2	—	75.0
p-Chlorophenyl	1.1	5	20.0	5.3	—	38.2
	5.0	30	6.0	19.0	—	65.0
Phenyl	1.1	4	12.1	2.2	trace of VIII	39.2
	5.0	30	—	40.0	—	53.3
p-Methoxyphenyl	1.1	5	14.7	10.9	—	44.6
	5.0	30	2.0	14.3	—	46.7
Picryl	5.0	120	—	11.9	21.1% of X	48.1

tained when large amounts of oxidizing agent were used for long period of oxidation. When nitro derivative of phenol (I: Ar=*p*-nitrophenyl) was treated with 7.5 mol of oxidizing agent, the resulting products were 4-nitrodiphenyl, molecular nitrogen and a red tarry compound. Disappearance of hydrazone (V) is due to its oxidative degradation since it has also an oxidizable phenol group. Thus, the oxidation of hydrazone (V) was carried out at 10 °C with an excess aqueous alkaline solution of potassium ferricyanide. The reaction proceeded slowly and evolution of nitrogen gas continued for several hours. The ESR spectra (Fig. 1) indicate that more than two species of stable free

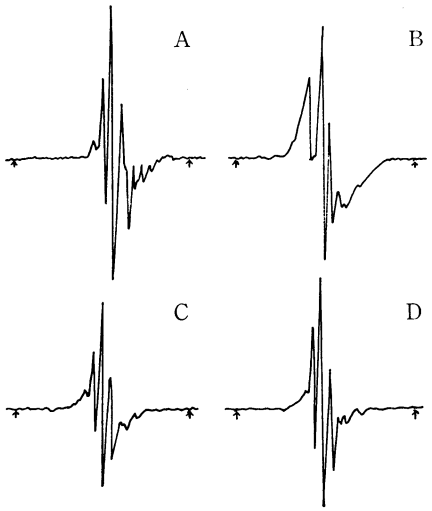


Fig. 1. ESR spectra observed in the oxidation of hydrazones (V).
A) V; Ar=*p*-nitrophenyl, B) V; Ar=*p*-chlorophenyl, C) V; Ar=phenyl, D) V; Ar=*p*-methoxyphenyl.
↑ : ESR signals of Fremy's salt as a marker (The center line is not shown).

radicals exist in the organic layer of the reaction mixture of hydrazone (V), and the location of the peaks in the ESR spectrum of each derivative of hydrazone (V) is the same as that observed in the oxidation of the corresponding derivative of phenol (I) (Fig. 2). Thus, it is very likely that the stable radicals observed in the oxidation of phenol (I) are not radical (II) but other radicals originating from hydrazone (V). One might be radical (VII), and the others might be some radicals possibly formed during the process of degradation of

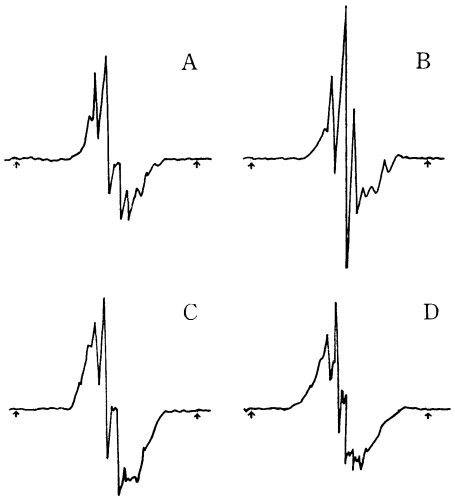


Fig. 2. ESR spectra observed in the oxidation of phenols (I)
A) I; Ar=*p*-nitrophenyl, B) I; Ar=*p*-chlorophenyl, C) I; Ar=phenyl, D) I; Ar=*p*-methoxyphenyl.
↑ : ESR signals of Fremy's salt as a marker (The center line is not shown.)

radical (VII). Diphenyl derivatives (VI), 2,6-di-*t*-butyl-*p*-benzoquinone (VIII), 3,3′,5,5′-tetra-*t*-butyldiphenoquinone (IX) and red tarry compound were obtained from the organic layer which had been kept standing for about four weeks to allow stable radicals to disappear (Table 2). The result shows that some

Table 2. Oxidation products of hydrazones (V)

Ar of (V)	Reaction time (hr)	Yields of oxidation products (%) (VI)	(VIII)	(IX)	N_2
p-Nitrophenyl	6.5	40.2	34.1	1.2	54.0
p-Chlorophenyl	5	21.1	20.5	1.7	71.0
Phenyl	4	16.2	25.0	0.7	65.0
p-Methoxyphenyl	3	16.3	22.7	0.5	60.0

parts of diphenyl derivative (VI) and 3,3′,5,5′-tetra-*t*-butyldiphenoquinone (IX) in the oxidation products of phenol (I) originated from hydrazone (V). The path of oxidation presumed from the isolated compounds is given in Fig. 3. Oxidizing agent will generate free radical (II) by the abstraction of a hydrogen atom from phenol (I). Radical (II) might disappear thorugh a few routes. One possible reaction is homolytic sub-

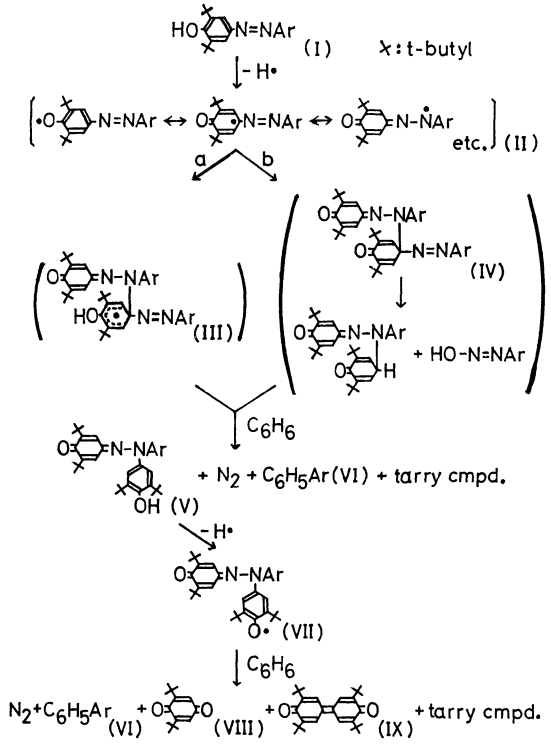


Fig. 3. Presumed reaction path.

stitution (route a). Radical (II) attacks phenol (I), and hydrazone (V) is formed from the intermediate (III) through elimination of arylazo radical, which gives out molecular nitrogen and diphenyl derivative (VI) through the reaction with benzene used as solvent. Another possible reaction is the recombination of radical (II) (route b). The self-coupling of radical (II) at carbon and nitrogen atom forms a dimer (IV), which is hydrolyzed to aryldiazonium hydroxide and hydrazone (V) *via* its dienone form. Aryldiazonium hydroxide undergoes decomposition to yield molecular nitrogen and diphenyl derivative (VI).[11] As for recombination reaction of radical (II), modes of coupling other than oxygen-oxygen coupling[12] and polymerization are possible since the maximum yield of molecular nitrogen based on the used phenol (I) is 75% and a large amount of tarry materials which may consist of the compounds through such a reaction path are obtained. Oxidizing agent will give a phenoxy radical (VII) by abstraction of a hydrogen atom from hydrazone (V), and radical (VII) will decompose to yield the final oxidation products (Table 2).

Picryl derivative of phenol (I; Ar=picryl) gave picrylbenzene (VI: Ar=picryl) and an anil derivative (X) instead of hydrazone (V). The strong electron-attracting power of picryl group might weaken and cleave the nitrogen-nitrogen bonding (=N–N<) of the dimer (IV), and an anil derivative might be formed as a result of the elimination of quinone-imino nucleus and picrylazo group.

11) W. E. Bachmann and R. A. Hoffman, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y. (1940), Vol. 2, p. 224.
12) T. Matsuura and A. Nishinaga, "Yuri-ki no Kagaku," ed. by H. Sakurai and K. Tokumaru, Nanko-do, Tokyo (1967), p. 176.

Experimental

4-Arylazo-2,6-di-t-butylphenols (I). Phenols (I) were prepared by the same method as reported previously.[1]

Oxidation of 4-Arylazo-2,6-di-t-butylphenols (I). An aqueous solution (0.2 mol/l) of potassium ferricyanide and potassium hydroxide was placed in a Schlenk tube equipped with a gas buret. A solution of phenol (I) in benzene was placed in another Schlenk tube. Both solutions were degassed three times by freezing with dry ice–acetone, then argon gas was led into both Schlenk tubes. While the temperature of each solution was kept at 10 °C, a benzene solution of phenol (I) was carefully added to the aqueous solution of the oxidizing agents. The mixture was then stirred for several minutes (Table 1), and the volume of evolved gas was determined with the gas buret in the course of stirring. The reaction was stopped by pouring the reaction mixture to degassed water in a separatory funnel of Schlenk type. The organic layer was washed with degassed water and dried over anhydrous sodium sulphate under the atmosphere of argon until the ESR spectrum showed almost complete absence of radical species in the organic layer. A tarry residual compound was obtained after distilling off benzene from the organic layer and the oxidation products of each phenol (I) were separated from the residual tarry compound according to the following.

Oxidation Products of 4-p-Nitrophenylazo-2,6-di-t-butylphenol (I: Ar=p-nitrophenyl) (1.75 g, 5.0 mmol) in benzene (200 ml): Yellow brown powder was obtained by washing the tarry compounds with cyclohexane, and yellow brown needles of nitro derivative of hydrazone (V: Ar=*p*-nitrophenyl) (0.76 g, 27.2%) were recrystallized from methanol solution of this powder. Mp 197.0—199.0 °C *m/e* 559.344 (M^+). Found: C, 72.22; H, 8.18; N, 7.51%. Calcd for $C_{34}H_{45}O_4N_3$: C, 72.96; H, 8.10; N, 7.32%. IR (KBr) cm^{-1}: 3630 (ν_{OH}), 3030, 2950 (ν_{CH}), 1640 ($\nu_{C=N}$), 1625 ($\nu_{C=O}$), 1610 ($\nu_{C=C}$), 1510, 1355 (ν_{NO_2}), 1260 (*t*-butyl), 845, 820 (δ_{CH}). 4-Nitrodiphenyl (VI: Ar=*p*-nitrophenyl) (0.15 g, 15.0%) was isolated from the filtrate. Mp 113.0—114.0 °C. (lit,[13] 114 °C). All the resulting filtrate and washing were collected and the solvent was completely distilled. Chromatographic separation of *n*-hexane solution of residual compound on a column of silica gel yielded some phenolic red brown tarry compound, a small amount of hydrazone, 4-nitrodiphenyl and 3,3′,5,5′-tetra-*t*-butyldiphenoquinone (IX) (1 mg) mp 247.0—248.0 °C (lit,[14] 247.0 °C) *m/e* 408.311 (M^+).

Oxidation Products of 4-p-Chlorophenylazo-2,6-di-t-butylphenol (I: Ar=p-chlorophenyl) (3.44 g, 10.0 mmol) in Benzene (50 ml): Yellow powder was obtained by washing the red brown tarry compound with *n*-hexane. By recrystallization of the powder from *n*-hexane solution, yellow needles of chloro derivative of hydrazone (V: Ar=*p*-chlorophenyl) (1.1 g, 20.0%) were obtained. Mp 203.0—205.0 °C. *m/e* 548.319 (M^+). Found: C, 74.05; H, 8.28; N, 5.15; Cl, 6.37%. Calcd for $C_{34}H_{45}O_2N_2Cl$: C, 74.36; H, 8.26; N, 5.10; Cl, 6.46%. IR (KBr) cm^{-1}: 3630 (ν_{OH}), 3030, 2950 (ν_{CH}), 1625 ($\nu_{C=N}$), 1615 ($\nu_{C=O}$), 1605 ($\nu_{C=C}$), 1260 (*t*-butyl), 880, 820 (δ_{CH}). Chromatographic separation of the washing on a column of alumina gave pale yellow plates of 4-chlorodiphenyl (VI: Ar=*p*-chlorophenyl) (0.1 g, 5.3%), mp 74.5—76.0 °C (lit,[13] 77.5 °C), a small amount of hydrazone and a red tarry compound.

Oxidation Products of 4-Phenylazo-2,6-di-t-butylphenol (I: Ar=phenyl) (3.10 g, 10.0 mmol) in Benzene (60 ml): Chromato-

13) "Handbook of Chemistry," ed. by N. A. Lange, McGraw-Hill Book Company, Inc., New York, N. Y. (1961), p. 382
14) H. Hart and F. Cassis, *J. Amer. Chem. Soc.*, **73**, 3179 (1951).

graphic separation of *n*-hexane solution of the red tarry compound gave colorless plates of diphenyl (VI: Ar=phenyl) (0.03 g, 2.2%), mp 69.0—69.5 °C (lit,[13] 70.5 °C), a red brown tarry compound and yellow brown plates of unsubstituted derivative of hydrazone (V: Ar=phenyl) (0.5 g, 12.1%), mp 151.0—153.0 °C. Found: C, 78.45; H, 8.86; N, 5.29%. Calcd for $C_{34}H_{46}O_2N_2$: C, 79.33; H, 9.01; N, 5.44%. IR (KBr) cm^{-1}: 3630 (ν_{OH}), 3030, 2950 (ν_{CH}), 1640 ($\nu_{C=N}$), 1620 ($\nu_{C=O}$), 1605 ($\nu_{C=C}$), 1255 (*t*-butyl), 880, 750 (δ_{CH}). A very small amount of 2,6-di-*t*-butyl-*p*-benzoquinone (VIII) was detected inside the flask containing the red brown tarry compound after it had been left standing for a long time. Mp 65.5—67.0 °C (lit,[15] 68.0 °C).

Oxidation Products of 4-p-Methoxyphenylazo-2,6-di-t-butylphenol (I: Ar=p-methoxyphenyl) (3.41 g, 10.0 mmol) in Benzene (50 ml): Yellow powder was obtained by washing the red brown tarry compound with *n*-hexane. By recrystallization of this powder from methanol solution, yellow plates of hydrazone (V: Ar=*p*-methoxyphenyl) (0.73 g, 14.7%) were obtained. Mp 181.0—182.0 °C, *m/e* 544.355 (M^+). Found: C, 76.65; H, 8.86; N, 4.89%. Calcd for $C_{35}H_{48}N_2O_3$: C, 77.16; H, 8.88; N, 5.14%. IR (KBr) cm^{-1}: 3630 (ν_{OH}), 3030, 2950 (ν_{CH}), 1625 ($\nu_{C=N}$), 1615 ($\nu_{C=O}$), 1610 ($\nu_{C=C}$), 1245 (*t*-butyl), 1020 (ν_{OMe}) 880, 825 (δ_{CH}). Chromatographic separation of the washing on a column of alumina gave yellow plates of 4-methoxydiphenyl (VI: Ar=*p*-methoxyphenyl) (0.2 g, 10.9 %), mp 87.0—88.0 °C (lit,[13] 90 °C), and a red brown tarry compound.

Oxidation Products of 4-Picrylazo-2,6-di-t-butylphenol (I: Ar=picryl) (0.41 g, 0.9 mmol) in Benzene (35 ml): Yellow brown powder was obtained by washing the red brown tarry compound with cyclohexane. Chromatographic separation of benzene solution of this powder on a column of silica gel gave a yellow compound, pale yellow plates of picrylbenzene (0.03 g, 11.9%) mp 130.0—131.5 °C (lit,[16] 130.0 °C), a small amount of starting material and a dark red tarry compound. Yellow plates of anil (X) (0.08 g, 19.1%) were recrystallized from methanol solution of the yellow compound. Mp 176.0—177.0 °C, *m/e* 430.152 (M^+). Found: C, 56.03; H, 4.91; N, 12.97%. Calcd for $C_{20}H_{22}O_7N_4$: C, 55.81; H, 5.15; N, 13.02%. IR (KBr) cm^{-1}: 3030, 2950 (ν_{CH}), 1660 ($\nu_{C=N}$), 1640 ($\nu_{C=O}$), 1620 ($\nu_{C=C}$), 1540, 1345 (ν_{NO_2}), 1250 (*t*-butyl), 880, 820 (δ_{CH}).

Oxidation of Hydrazone (V). A solution of hydrazone (V) (1.0 mmol) in benzene (60 ml) was oxidized with an aqueous alkaline solution of potassium ferricyanide (5.0 ml) at 10 °C until cessation of nitrogen gas evolution, and the reaction mixture was treated in the same way as in the oxidation of phenols (I). The solvent was distilled off after the stable radicals in the organic layer had disappeared, and isolation of oxidation products from the residual compounds was carried out as described below.

Oxidation Products of Nitro Derivative of Hydrazone (V: Ar=p-nitrophenyl): The yellow brown residual compound was dissolved in *n*-hexane and a small amount of insoluble material remained. The starting material (9 mg, 1.6%) was obtained by recrystallization of this insoluble material from methanol solution. The *n*-hexane solution was passed through a column of alumina, and 3,3′,5,5′-tetra-*t*-butyldiphenoquinone (X) (5 mg, 1.2%), 2,6-di-*t*-butyl-*p*-benzoquinone (VIII) (75 mg, 34.1%), 4-nitrodiphenyl (VI: Ar=*p*-nitrophenyl) (80 mg, 40.2%) and a red brown tarry compound were obtained.

Oxidation Products of Chloro Derivative of Hydrazone (V: Ar=p-chlorophenyl): The red brown residual compound was dissolved in *n*-hexane and passed through a column of alumina. 4-Chlorodiphenyl (VI: Ar=*p*-chlorophenyl) 40 mg, 21.1%), 3,3′,5,5′-tetra-*t*-butyldiphenoquinone (IX) (7 mg, 1.7%), 2,6-di-*t*-butyl-*p*-benzoquinone (VIII) 45 mg, 20.5%) and a red brown tarry compound were obtained.

Oxidation Products of Unsubstituted Derivative of Hydrazone (V: Ar=phenyl): The red brown residual compound was dissolved in *n*-hexane and passed through a column of alumina. Diphenyl (VI: Ar=phenyl) (25 mg, 16.2%), 3,3′,5,5′-tetra-*t*-butyldiphenoquinone (VIII) (3 mg, 0.7%), 2,6-di-*t*-butyl-*p*-benzoquinone (VIII) (55 mg, 25.0%) and a red brown tarry compound were obtained.

Oxidation Products of Methoxy Derivative of Hydrazone (V: Ar=p-methoxyphenyl): Red brown residual compound was dissolved in *n*-hexane and passed through a column of alumina. 3,3′,5,5′-Tetra-*t*-butyldiphenoquinone (IX) (2 mg, 0.5%) was obtained from the first yellow band. The eluent from the second yellow brown band was passed through a column of silica gel, and 4-methoxydiphenyl (VI: Ar=*p*-methoxydiphenyl) (30 mg, 16.3%), 2,6-di-*t*-butyl-*p*-benzoquinone (VIII) (50 mg, 22.7%) and a red brown tarry compound were obtained.

All the melting points were uncorrected. The infrared spectra were taken with a Shimadzu IR-27G grating spectrophotometer. The ESR spectra for the benzene-diluted organic layer of the reaction mixture, which had been dried over anhydrous sodium sulphate for a few minutes directly following cessation of oxidation, were taken with a Hitachi 771 electron spin resonance spectrometer.

The author is indebted to Mr. Wasada for the mass spectra.

15) M. S. Kharash and B. S. Joshi, *J. Org. Chem.*, **27**, 651 (1962).
16) H. C. Gull and E. E. Turner, *J. Chem. Soc.*, **1929**, 498.