Reduction of Quinones and Quinonemonosulfonimides with *N,N*-Diethylhydroxylamine

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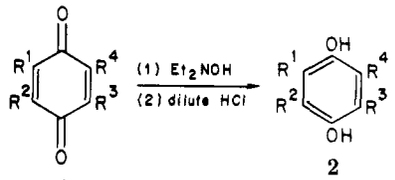
Quinones (1) and quinonemonosulfonimides (**3a–e** and **5**) are reduced with *N,N*-diethylhydroxylamine (DEH) to give the corresponding hydroquinones (**2**) and sulfonylaminophenols (**4a–e** and **6**), respectively. The DEH reduction is a key step in an improved synthetic route to dye developers (**11a–c** and **12a–c**). Nitrone–hydroquinone 1:1 complexes (**14a–f**) are isolated as intermediates.

Various reagents have been used for reduction of quinones to hydroquinones. For example, tin(II) chloride,[1] zinc and acetic acid,[2] iron and hydrochloric acid,[3] sodium dithionite,[4] sodium borohydride,[5] ascorbic acid,[6] polymethylhydrosiloxane,[7] molecular hydrogen,[8] and vanadium(II) chloride[9] have been reported as reducing agents for quinones. However, their reactions are often difficult to control when starting quinones contain other reducible (e.g., azo) and/or labile (e.g., acetoxyl) groups. More selective reducing agents must be developed for the synthesis of dye developers, which are azo dyes having a hydroquinone moiety used in diffusion transfer reversal (DTR) photography. Although molecular hydrogen has been used as a selective reducing agent in such synthesis,[10] excess hydrogen would cleave the azo groups. In the present work,[11] *N,N*-diethylhydroxylamine (DEH)[12] has been found to be a selective reducing agent for quinones and to be especially useful for preparation of the dye developers.

DEH Reduction of Quinones and Quinonemonosulfonimides. Table I summarizes the results of the DEH reduction of 1,4-benzoquinones (1) and 1,4-naphthoquinones (Scheme I). The reduction proceeds smoothly under almost neutral conditions and affords good yields of hydroquinones of a wide range. Monoalkyl- and monoaryl-substituted 1,4-benzoquinones can be readily reduced at room temperature. Further substitution of electron-donating groups tends to decrease the reactivity of benzoquinone nuclei. However, even tetramethyl-1,4-benzoquinone can be reduced at an elevated temperature. The reactivity of the 1,4-benzoquinones may be correlated to their half-wave potentials ($E_{1/2}$) obtained by polarographic measurements. The $E_{1/2}$ values (vs. SCE) of most 1,4-benzoquinones containing electron-donating substituents have been found to be in the range of −0.025 (unsubstituted 1,4-benzoquinone) to −0.260 V (tetramethyl-1,4-benzoquinone).[13] The $E_{1/2}$ value of DEH is presumed to be approximately equal to that of *N,N*-dibenzylhydroxylamine (−0.38 V),[14] which is low enough to reduce most 1,4-benzoquinones. Electron-attracting substituents increase the reactivity of quinone nuclei, which are more smoothly reduced than 1,4-benzoquinone itself.

o- and *p*-quinonemonosulfonimide derivatives also are reduced with DEH as shown in Table II and Scheme II. The corresponding *o*- and *p*-sulfonylaminophenols are obtained in good yields under mild conditions. Although arylhydrazines have been used in the reduction of quinonemonosulfonimides,[15] the results in Table II indicate

Scheme I



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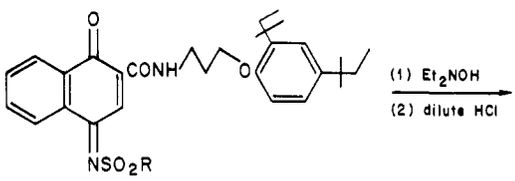
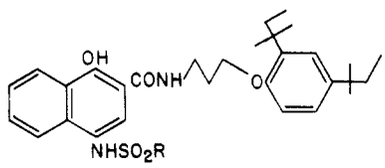
Scheme II



3a, R = $(CH_2)_3OC_6H_4NO_2$-*p*
b, R = Ph
c, R = $C_6H_4CH_3$-*p*
d, R = C_6H_4Cl-*p*
e, R = $C_6H_4NHCOCH_3$-*p*



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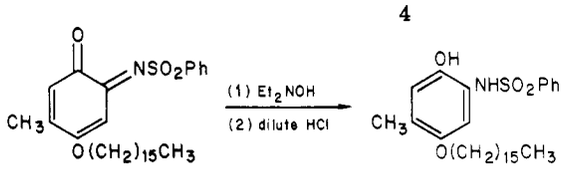

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(4) G. A. Reynolds and J. A. VanAllan, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 15; H. Otomasu, *Chem. Pharm. Bull.*, **16**, 378 (1968).
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(7) J. Lipowitz and S. A. Bowman, *J. Org. Chem.*, **38**, 162 (1973).
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(9) T.-L. Ho and G. A. Olah, *Synthesis*, 815 (1976).
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Table I. Reduction of Quinones with DEH

quinone (1)				reacn	hydroquinone (2)[b]	
R^1	R^2	R^3	R^4	condition[a]	yield, %	mp, °C
H	H	H	H	A	66	170-171
CH_3	H	H	H	A	43	124-125
t-Bu	H	H	H	A	62	128-129
Ph	H	H	H	A	81	97-98
p-$CH_3C_6H_4$	H	H	H	A	83	120-121
p-$EtOCOC_6H_4$	H	H	H	A	82	113-117
p-$CH_3COC_6H_4$	H	H	H	A	75	197.5-198
p-ClC_6H_4	H	H	H	A	82	117-118.5
o-ClC_6H_4	H	H	H	A	54	114-115
p-BrC_6H_4	H	H	H	A	60	134-135
p-$O_2NC_6H_4$	H	H	H	A	77	217-221
m-$O_2NC_6H_4$	H	H	H	A	71	138-142
CH_3	CH_3	H	H	A	42	*c*
t-Bu	H	*t*-Bu	H	B	68	219-220
Cl	H	H	Cl	A	68	162-163
CH_3	CH_3	CH_3	H	B	66	172-173
CH_3	CH_3	CH_3	CH_3	B	81	240-243[d]
CH_3	CH_3	CH_3	Br	B	82	170-172[e]
Cl	Cl	Cl	Cl	A	95	243-245[f]
Cl	Cl	CN	CN	A	76	>290
CH=CHCH=CH		H	H[g]	B	83	165-167

[a] Condition A, stirred in ethyl acetate at room temperature; condition B, refluxed in ethyl acetate. [b] Identified with an authentic sample. [c] Sublimed on melting point measurement. [d] Sintered at 235 °C. [e] Decomposed. [f] Sintered at 236 °C. [g] 1,4-Naphthoquinone.

Table II. Reduction of Quinonemonosulfonimides with DEH[a]

substrate	yield, %	product[b]	mp, °C
3a	74	**4a**	169-171
3b	87	**4b**	174-177
3c	71	**4c**	186-188
3d	71	**4d**	191-192
3e	67	**4e**	203-205
5	74	**6**	97-98

[a] The reactions were effected in ethyl acetate at room temperature. [b] Satisfactory analytical values (±0.3% C, H, N) were reported for all compounds.

Table III. DEH Reduction for Preparing Dye Developers[a]

substrate	yield, %	product[b]	mp, °C
9a	80	**11a**	222-224
9b	66	**11b**	176-178
9c	85	**11c**	142-144
10a	70	**12a**	161-162 dec
10b	83	**12b**	168-169
10c	82	**12c**	172-173 dec

[a] All substrates were reduced with DEH at room temperature. [b] Satisfactory analytical values (±0.3% C, H, N) were reported for all compounds.

Table IV. 1:1 Nitrone-Hydroquinone Complexes

compd[a]	yield, %	mp, °C	yield of hydroquinone, %
14a	93	97-98	75
14b	93	74-76	54
14c	62	99-101	91
14d	80	85-87	68
14e	71	214-216	90
14f	57	164-177	81

[a] Satisfactory analytical values (±0.3% C, H, N) were reported for all compounds.

the usefulness and convenience of the DEH reduction. Compounds represented by the formulas **4** and **6**, wherein group R or Ph is displaced by a dye moiety, have been disclosed as diffusible dye releasing redox (DRR) compounds utilized in DTR photography.[16] Scheme II suggests that DEH can be used as an antioxidant for such DRR compounds, since DEH may be oxidized with oxygen before the DRR compounds.

Application of the DEH Reduction to the Synthesis of Dye Developers. Table III and Scheme III show the usefulness of DEH reduction in the synthesis of dye developers. An improved and short-cut route[17] is developed by the introduction of the selective DEH reduction and so-called diazoxidation of aniline having a hydroquinone moiety (**7**). Treatment of starting material (**7**) with sodium nitrite and hydrochloric acid resulted in oxidation of the hydroquinone moiety and diazotization of the amino group simultaneously. The resulting intermediate (**8**) is appreciably stable under acidic conditions, although it possesses both a diazonium and a quinone group in the molecule.[18] The diazonium salt (**8**) couples with 4-alkoxy-1-naphthols to yield the corresponding azo dyes having a quinone moiety (**9**). Acetylation of **9** with isopropenyl acetate in the presence of an acid catalyst gives compounds **10** having temporarily shifted visible absorption. Dye developers (**11**) and temporarily shifted dye developers (**12**) are obtained by the DEH reduction of **9** and **10**, respectively, in good yields as shown in Table III. Azo groups in the substrates (**9** and **10**) are not affected through the DEH reduction. Acetoxyl groups of **10** are also unchanged under the condition of the DEH reduction. However, DEH reduction of **13** is accompanied by partial hydrolysis of its acetoxyl group. This fact may be attributed to the weakly basic character of DEH.

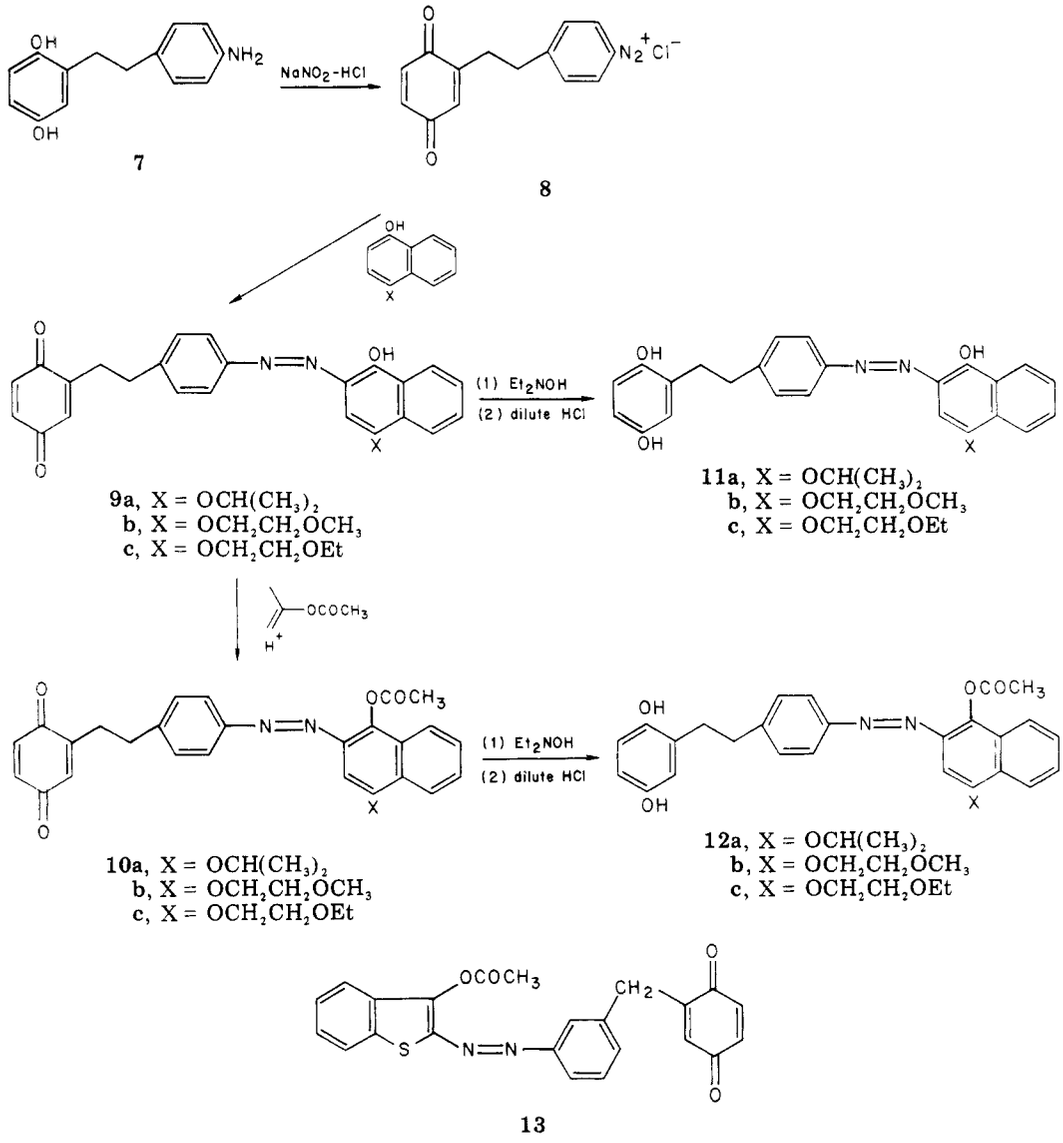
Isolation of 1:1 Nitrone-Hydroquinone Complexes. DEH itself is considered to be converted into the corresponding nitrone in the process of the reduction. The nitrone has been reported to be formed by the oxidation of DEH with *tert*-butyl hydroperoxide[19] or nickel per-

(16) L. J. Fleckenstein and J. Figueras, U.S. Patent B351 673 (1975); L. J. Fleckenstein, U.S. Patent 3 928 312 (1975).

(17) For the previous method of preparing dye developers, see S. M. Bloom, M. Green, M. Idelson, and M. S. Simon in "The Chemistry of Synthetic Dyes", K. Venkataraman, Ed., Vol. 8, Academic Press, New York, N.Y., 1978, p 331.

(18) Reaction of 1,4-benzoquinones with diaonium salts has been reported. See, D. E. Kvalnes, *J. Am. Chem. Soc.*, **56**, 2478 (1934).

Scheme III



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9a, X = $OCH(CH_3)_2$
b, X = $OCH_2CH_2OCH_3$
c, X = OCH_2CH_2OEt

11a, X = $OCH(CH_3)_2$
b, X = $OCH_2CH_2OCH_3$
c, X = OCH_2CH_2OEt

10a, X = $OCH(CH_3)_2$
b, X = $OCH_2CH_2OCH_3$
c, X = OCH_2CH_2OEt

12a, X = $OCH(CH_3)_2$
b, X = $OCH_2CH_2OCH_3$
c, X = OCH_2CH_2OEt

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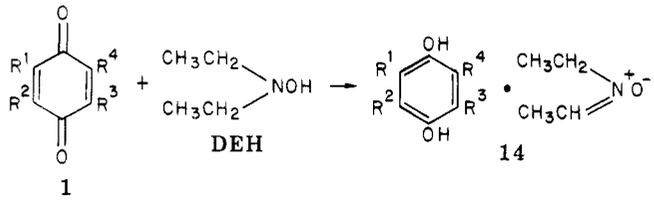
Scheme IV



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a, $R^1 = C_6H_4CH_3$-*p*, $R^2 = R^3 = R^4 = H$
b, $R^1 = Ph$, $R^2 = R^3 = R^4 = H$,
c, $R^1 = C_6H_4Cl$-*p*, $R^2 = R^3 = R^4 = H$
d, $R^1 = C_6H_4Br$-*p*, $R^2 = R^3 = R^4 = H$
e, $R^1 = R^3 = t$-Bu, $R^2 = R^4 = H$
f, $R^1 = R^2 = R^3 = R^4 = Cl$

oxide[20] and trapped with methyl methacrylate to give an isoxazolidine adduct. In the DEH reduction of the present work, the nitrone forms complexes (**14**) with the resulting hydroquinones which are decomposed by treatment with dilute acid (Scheme IV). For example, the complex (**14a**) between 2-(*p*-tolyl)hydroquinone and the nitrone is precipitated as white crystals, when DEH reduction of 2-(*p*-tolyl)-1,4-benzoquinone is performed in benzene.[21] Elemental analysis of the crystals gives the molecular formula of $C_{17}H_{21}NO_3$ which is consistent with a 1:1 nitrone–hydroquinone complex. Its IR spectrum shows a characteristic band of a nitrone group at 1638 cm^{-1}. The ^1H NMR spectrum of **14a** (in $(CD_3)_2SO$) exhibits a quartet at δ 6.98 (CH=, J = 6 Hz) and a doublet at δ 1.79 (CH_3CH=, J = 6 Hz), which reveal the presence of a nitrone moiety. Irradiation of the doublet signal at δ 1.79 causes the decoupling of the methine quartet at δ 6.98 to afford a broad singlet. The presence of a nitrone moiety is indicated also by the fact that **14a** is formed by the reaction of 2-(*p*-tolyl)hydroquinone with the nitrone, which is prepared by the oxidation of DEH with manganese dioxide.

Several nitrone–hydroquinone complexes (**14a–f**) are isolated as crystalline products (Table IV and Scheme IV). The characteristic methine quartets also are observed at δ 6.9–7.1. Appearance of the signals of the methine protons in the region of aromatic protons may be ascribed to the

(19) H. E. De La Mare and G. M. Coppinger, *J. Org. Chem.*, **28**, 1068 (1963).
(20) K. Nakagawa, H. Onoue, and K. Minami, *Chem. Pharm. Bull.*, 17, 835 (1969).

(21) A 1:1 complex of a cyclic nitrone and hydroquinone has been reported in E. J. Alford, J. A. Hall, and M. A. T. Rogers, *J. Chem. Soc. C*, 1103 (1966); M. A. T. Rogers, *Nature (London)*, 177, 128 (1956).

Table V. Yields and Analytical Data of Quinonemonosulfonimides

compd	yield, %	mp, °C	calcd			found		
			% C	% H	% N	% C	% H	% N
3a	43	131–132[a]	65.3	6.6	5.9[b]	65.4	6.6	5.7
3b	39	116–119	70.3	6.9	4.6[c]	70.1	7.0	4.7
3c	51	118–121	70.7	7.1	4.5[d]	70.9	7.0	4.5
3d	48	139–146	66.6	6.4	4.3[e]	66.4	6.5	4.1
3e	77	195–197	67.9	6.8	6.3[f]	68.0	6.7	6.3
5	80	103–105	69.4	8.6	2.8[g]	69.6	8.7	2.8

[a] Sintered at 122 °C. [b] $C_{39}H_{47}N_3O_8S$. [c] $C_{36}H_{42}N_2O_5S$. [d] $C_{37}H_{44}N_2O_5S$. [e] $C_{36}H_{41}ClN_2O_5S$. [f] $C_{38}H_{45}N_3O_6S$. [g] $C_{29}H_{43}NO_4S$.

effect of the positively charged nitrogen.

Attempted isolation of the nitrone complexes of 2-methyl-, 2-*tert*-butyl-, 2,3-dimethyl-, tetramethyl-, 2-bromo-3,5,6-trimethyl-, 2,3-dichloro-5,6-dicyano-, and 2-(*o*-chlorophenyl)hydroquinone proves futile.

Acid treatment of **14a–f** affords the corresponding hydroquinones in good yields as shown in Table IV. This fact reveals the presence of a hydroquinone moiety in the complexes and proves the validity of Scheme IV.

Experimental Section

Infrared spectra were measured with a JASCO IRA-2 diffraction grating infrared spectrophotometer. ^1H NMR spectra were obtained by using Varian EM-390 90-MHz NMR spectrometers. Chemical shifts are expressed in parts per million downfield from internal tetramethylsilane. Melting points are uncorrected.

Reduction of Quinones (1) with DEH. Condition A. DEH (2.50 g, 0.028 mol) was added to a stirred suspension of 2-(*p*-tolyl)-1,4-benzoquinone (4.95 g, 0.025 mol) in ethyl acetate (50 mL) at room temperature. The resulting solution was stirred for 40 min, washed successively with ca. 4% HCl and with water, and dried over anhydrous Na_2SO_4. Concentration and recrystallization from a mixture of benzene and *n*-hexane (1:8) gave 2-(*p*-tolyl)-hydroquinone (4.10 g, 83%); mp 120–121 °C.

Most 1,4-benzoquinones were reduced under condition A. Yields and melting points are collected in Table I.

Condition B. A mixture of 2-bromo-3,5,6-trimethyl-1,4-benzoquinone (1.15 g, 0.0050 mol), DEH (0.50 g, 0.0056 mol), and ethyl acetate (20 mL) was heated under reflux for 2 h. The reaction mixture was cooled and washed twice with ca. 4% HCl and then with saturated aqueous NaCl solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Recrystallization from benzene–*n*-hexane (1:5) gave 2-bromo-3,5,6-trimethylhydroquinone (0.95 g, 82%); mp 170–172 °C dec.

Reduction of other benzoquinones under condition B are collected in Table I.

Reduction of Quinonemonosulfonimides (3 and 5) with DEH. DEH (0.54 g, 0.0060 mol) was added in one portion to a stirred solution of 2-[*N*-3-(2,4-di-*tert*-pentylphenoxy)propylcarbamoyl]-1,4-naphthoquinone-4-benzenesulfonimide (**3b**) (0.92 g, 0.0015 mol) in ethyl acetate (20 mL) at room temperature. The reaction mixture was stirred for 2 h and worked up as described above. Recrystallization from benzene–*n*-hexane (1:2) gave 4-benzenesulfonylamino-2-[*N*-3-(2,4-di-*tert*-pentylphenoxy)-propylcarbamoyl]-1-naphthol (**4b**) (0.80 g, 87%); mp 174–177 °C.

Other quinonemonosulfonimides (**3** and **5**) were reduced by similar methods. The results are collected in Table II.

Preparation of *o*- and *p*-Sulfonylaminophenols (4 and 6) from *o*- and *p*-Aminophenols. Pyridine (15 mL) was added at 20 °C to a stirred solution of 4-amino-2-[*N*-3-(2,4-di-*tert*-pentylphenoxy)propylcarbamoyl]-1-naphthol $^1/_2H_2SO_4$ salt (**15**) (53.0 g, 0.10 mol)[22] and 3-(4-nitrophenoxy)propanesulfonyl chloride[22] (19.4 g, 0.11 mol) in tetrahydrofuran (150 mL). The mixture was stirred for 1.5 h at 20 °C and poured into dilute HCl. The precipitates were collected and recrystallized from ethano to give **4a** (42.5 g, 59%); mp 169–171 °C. The compound was identified with the sample prepared by DEH reduction described above.

Other *p*-sulfonylaminophenols (**4**) were obtained by similar reactions of **15** with the corresponding sulfonyl chlorides. The yields were 72% for **4b**, 42% for **4c**, 62% for **4d**, and 62% for **4e**. Compound **6** was obtained similarly by the reaction of 2-amino-4-hexadecyloxy-5-methylphenol hydrochloride[23] with benzenesulfonyl chloride in a 64% yield.

Preparation of Quinonemonosulfonimides (3). A suspension of **4a** (10.0 g, 0.014 mol) and manganese dioxide (40.0 g) in chloroform (150 mL) was stirred for 4 h at room temperature. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was recrystallized from a mixture of ethyl acetate (5 mL) and *n*-hexane (50 mL) to give golden yellow crystals of **3a** (4.30 g, 43%); mp 131–132 °C (sintered at 122 °C).

Other quinonemonosulfonimides (**3b–e** and **5**) were prepared by similar methods. The results and elemental analyses are collected in Table V.

Preparation of Azo Dyes Having a Quinone Moiety (9). (A) Diazoxidation of 2-[2-(4-Aminophenyl)ethyl]hydroquinone (7). An aqueous solution (150 mL) of $NaNO_2$ (11.0 g, 0.16 mol) was added dropwise to a stirred solution of **7**[24] (13.3 g, 0.050 mol) in 2.5% HCl (600 mL) at −5 to 0 °C over 20 min. The mixture was stirred for 2 h below 3 °C. A 1.0-g portion of sulfamic acid was added to this mixture to decompose the excess nitrous acid. Then, sodium acetate (45.0 g) was added to adjust the pH of the mixture to about 4.

(B) Coupling Reactions. The resulting solution of diazonium salt (**8**) was added dropwise to an ethanolic solution (500 mL) of 4-isopropoxy-1-naphthol (10.1 g, 0.050 mol) below 10 °C. A saturated aqueous $NaHCO_3$ solution (400 mL) was added, and the mixture was stirred for 1.5 h at room temperature. The crystals precipitated were collected by filtration, air-dried, and recrystallized from a benzene–methanol mixture (4:3) to yield azo dye **9a** (11.2 g, 52%); mp 168–170 °C.

Compounds **9b,c** were obtained similarly by the above-mentioned method. The results and analytical data are found in Table VI.

Acetylation of Hydroxyl Groups of Azo Dyes (9). A mixture of 4-isopropoxy-2-[4-(2-quinonylethyl)phenylazo]-1-naphthol (**10a**) (88.0 g, 0.20 mol), isopropenyl acetate (240 mL), 1,2-dichloroethane (1000 mL), and sulfuric acid (1.5 mL) was heated under reflux for 45 min. The reaction mixture was cooled, washed three times with water, and dried over anhydrous Na_2SO_4. After treatment with activated carbon, the mixture was concentrated in vacuo. The residue was recrystallized from a mixture of benzene (100 mL) and *n*-hexane (140 mL) to give an azo dye having shifted visible absorption (**10a**) (59.0 g, 61%); mp 135–137 °C.

Similarly, compound **10b,c** were obtained by the above-described procedure. The results and analytical data are shown in Table VII.

Preparation of Dye Developers (11 and 12) by DEH Reduction. A solution of DEH (1.00 g, 0.011 mol) in ethyl acetate (20 mL) was added at room temperature to a stirred solution of **9a** (4.40 g, 0.010 mol) in ethyl acetate (80 mL). The reaction mixture was stirred for 2 h at room temperature, washed successively with ca. 4% HCl and with a saturated aqueous NaCl

(22) S. Fujita, Y. Maekawa, S. Ono, S. Yokoyama, K. Inoue, and Y. Yoshida, Japan Kokai, 52-106 727 (1977).

(23) K. Koyama, Y. Maekawa, and M. Miyagawa, U.S. Patent 4 055 428 (1977).

(24) E. R. Blout, M. Green, H. G. Rogers, M. S. Simon, and R. B. Woodward, U.S. Patent 3 019 107 (1962).

Table VI. Yields and Analytical Data of Azo Dyes (9)

compd	yield, %	mp, °C	calcd % C	calcd % H	calcd % N	found % C	found % H	found % N
9a	52	168-170	73.6	5.5	6.4[a]	73.6	5.4	6.3
9b	51	167-169	71.0	5.3	6.1[b]	71.0	5.3	6.2
9c	55	148-149	71.5	5.6	6.0[c]	71.5	5.5	6.1

[a] $C_{27}H_{24}N_2O_4$. [b] $C_{27}H_{24}N_2O_5$. [c] $C_{28}H_{26}N_2O_5$.

Table VII. Yields and Analytical Data of 10

compd	yield, %	mp, °C	calcd % C	calcd % H	calcd % N	found % C	found % H	found % N
10a	61	135-137	72.2	5.4	5.8[a]	72.4	5.6	5.5
10b	72	149-150	69.9	5.3	5.6[b]	70.0	5.3	5.4
10c	82	130-132	70.3	5.5	5.5[c]	70.6	5.5	5.8

[a] $C_{29}H_{26}N_2O_5$. [b] $C_{29}H_{26}N_2O_6$. [c] $C_{30}H_{28}N_2O_6$.

solution, and dried over anhydrous Na_2SO_4. The mixture was concentrated and the residue was recrystallized from ethanol to afford **11a** (3.50 g, 80%); mp 222–224 °C.

Preparation of other dye developers is summarized in Table III.

Preparation of 1:1 Nitrone–Hydroquinone Complexes (14). DEH (2.50 g, 0.028 mol) was added at room temperature to a solution of 2-(*p*-tolyl)-1,4-benzoquinone (4.95 g, 0.025 mol) in benzene (50 mL) and stirred for 1 h. Crystallization from the reaction mixture was induced by scratching the flask. The precipitates were collected and washed with benzene. Drying under vacuum gave compound **14a** as white crystals (6.72 g, 93%): mp 97–98 °C; IR (Nujol) 1638 (CH=N) cm^{-1}; NMR ($(CD_3)_2SO$) δ 1.26 (3 H, t, J = 8 Hz, CH_3CH_2), 3.69 (2 H, q, J = 8 Hz, CH_3CH_2), 1.79 (3 H, d, J = 6 Hz, CH_3CH=), 6.98 (1 H, q, J = 6 Hz, CH_3CH=), 8.68 (2 H, s, OH), 6.8–6.4 (ca. 3 H, hydroquinone nucleus H), 7.02 and 7.51 (4 H, AB q, J_{AB} = 8 Hz, phenyl H), 2.31 (3 H, s, CH_3).

Other nitrone–hydroquinone complexes except **14e** were obtained by the above-described reactions at room temperature. The results are collected in Table IV.

14b: IR (Nujol) 1638 (CH=N) cm^{-1}; NMR ($(CD_3)_2SO$) δ 1.27 (3 H, t, J = 8 Hz, CH_3CH_2), 3.66 (2 H, q, J = 8 Hz, CH_3CH_2), 1.79 (3 H, d, J = 6 Hz, CH_3CH=), 6.90 (1 H, q, J = 6 Hz, CH_3CH=), 8.63 (2 H, s, OH), 6.9–6.4 (3 H, hydroquinone nucleus H), 7.7–7.2 (5 H, m, Ph).

14c: IR (Nujol) 1636 (CH=N) cm^{-1}; NMR ($(CD_3)_2SO$) δ 1.30 (3 H, t, J = 8 Hz, CH_3CH_2), 3.68 (2 H, q, J = 8 Hz, CH_3CH_2), 1.81 (3 H, d, J = 6 Hz, CH_3CH=), 7.00 (1 H, q, J = 6 Hz, CH_3CH=), 8.84 and 8.77 (2 H s + s, OH), 6.9–6.4 (3 H, m, hydroquinone nucleus H), 7.31 and 7.63 (4 H, AB q, J_{AB} = 9 Hz, phenyl H).

14d: IR (Nujol) 1639 (CH=N) cm^{-1}; NMR ($(CD_3)_2SO$) δ 1.28 (3 H, t, J = 7 Hz, CH_3CH_2), 3.72 (2 H, q, J = 7 Hz, CH_3CH_2), 1.80 (3 H, d, J = 6 Hz, CH_3CH=), 7.04 (1 H, q, J = 6 Hz, CH_3CH=), 8.91 and 8.84 (2 H, s + s, OH), 6.9–6.5 (3 H, m, hydroquinone nucleus H), 7.45 and 7.59 (4 H, AB q, J_{AB} = 8 Hz, phenyl H).

14f: IR (Nujol) 1655 (CH=N) cm^{-1}; NMR ($(CD_3)_2SO$) δ 1.25 (3 H, t, J = 7 Hz, CH_3CH_2), 3.69 (2 H, q, J = 7 Hz, CH_3CH_2), 1.77 (3 H, d, J = 6 Hz, CH_3CH=), 6.99 (1 H, q, J = 6 Hz, CH_3CH=), 3.29 (2 H, broad s, OH).

The 1:1 complex (**14e**) of the nitrone and 2,5-di-*tert*-butylhydroquinone was obtained by heating a mixture of DEH and 2,5-di-*tert*-butylbenzoquinone at 50 °C: IR (Nujol) 1627 (CH=N) cm^{-1}; NMR ($(CD_3)_2SO$) δ 1.26 (overlapped with *t*-Bu, t, J = 7 Hz, CH_3CH_2), 3.66 (2 H, q, J = 7 Hz, CH_3CH_2), 1.77 (3 H, d, J = 6 Hz, CH_3CH=), 6.91 (1 H, q, J = 6 Hz, CH_3CH=), 8.20 (2 H, s, OH), 6.49 (2 H, s, hydroquinone nucleus H), 1.46 (overlapped, s, *t*-Bu).

Reaction of the Nitrone Prepared in situ with 2-(*p*-Tolyl)hydroquinone. Manganese dioxide (0.87 g, 0.010 mol) was added to a solution of DEH (0.45 g, 0.0050 mol) in benzene (20 mL) at room temperature. The resulting suspension was stirred for 2 h and then filtered. The filtrate was added to a solution of 2-(*p*-tolyl)hydroquinone (1.00 g, 0.0050 mol) in benzene (20 mL). The reaction mixture was cooled and the flask was scratched to induce crystallization of **15a** (0.60 g, 42%), which was identical with the sample described above.

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Registry No. **1a**, 30237-07-1; **1b**, 363-03-1; **1c**, 20307-43-1; **1d**, 30100-33-5; **1e**, 2460-77-7; **1f**, 118-75-2; **1** (R^1 = R^2 = R^3 = R^4 = H), 106-51-4; **1** (R^1 = CH_3, R^2 = R^3 = R^4 = H), 553-97-9; **1** (R^1 = *t*-Bu, R^2 = R^3 = R^4 = H), 3602-55-9; **1** (R^1 = *p*-EtOCOC$_6$H$_4$, R^2 = R^3 = R^4 = H), 70524-41-3; **1** (R^1 = *p*-$CH_3COC_6H_4$, R^2 = R^3 = R^4 = H), 1921-32-0; **1** (R^1 = *o*-ClC_6H_4, R^2 = R^3 = R^4 = H), 84-25-3; **1** (R^1 = *p*-$O_2NC_6H_4$, R^2 = R^3 = R^4 = H), 15394-91-9; **1** (R^1 = *m*-$O_2NC_6H_4$, R^2 = R^3 = R^4 = H), 3844-86-8; **1** (R^1 = R^2 = CH_3, R^3 = R^4 = H), 526-86-3; **1** (R^1 = R^4 = Cl, R^2 = R^3 = H), 697-91-6; **1** (R^1 = R^2 = R^3 = CH_3, R^4 = H), 935-92-2; **1** (R^1 = R^2 = R^3 = R^4 = CH_3), 527-17-3; **1** (R^1 = R^2 = R^3 = CH_3, R^4 = Br), 7210-68-6; **1** (R^1 = R^2 = Cl, R^3 = R^4 = CN), 84-58-2; **1** (R^1, R^2 = CH=CH—CH=CH, R^3 = R^4 = H), 130-15-4; **2** (R^1 = R^2 = R^3 = R^4 = H), 123-31-9; **2** (R^1 = CH_3, R^2 = R^3 = R^4 = H), 95-71-6; **2** (R^1 = *t*-Bu, R^2 = R^3 = R^4 = H), 1948-33-0; **2** (R^1 = Ph, R^2 = R^3 = R^4 = H), 1079-21-6; **2** (R^1 = *p*-$CH_3C_6H_4$, R^2 = R^3 = R^4 = H), 10551-32-3; **2** (R^1 = *p*-EtOCOC$_6$H$_4$, R^2 = R^3 = R^4 = H), 70524-42-4; **2** (R^1 = *p*-$CH_3COC_6H_4$, R^2 = R^3 = R^4 = H), 3948-13-8; **2** (R^1 = *p*-ClC_6H_4, R^2 = R^3 = R^4 = H), 10551-37-8; **2** (R^1 = *o*-ClC_6H_4, R^2 = R^3 = R^4 = H), 117-71-5; **2** (R^1 = *p*-BrC_6H_4, R^2 = R^3 = R^4 = H), 70524-43-5; **2** (R^1 = *p*-$O_2NC_6H_4$, R^2 = R^3 = R^4 = H), 3844-85-7; **2** (R^1 = *m*-$O_2NC_6H_4$, R^2 = R^3 = R^4 = H), 59007-05-5; **2** (R^1 = R^2 = CH_3, R^3 = R^4 = H), 608-43-5; **2** (R^1 = R^3 = *t*-Bu, R^2 = R^4 = H), 88-58-4; **2** (R^1 = R^4 = Cl, R^2 = R^3 = H), 20103-10-0; **2** (R^1 = R^2 = R^3 = CH_3, R^4 = H), 700-13-0; **2** (R^1 = R^2 = R^3 = R^4 = CH_3), 527-18-4; **2** (R^1 = R^2 = R^3 = CH_3, R^4 = Br), 39055-45-3; **2** (R^1 = R^2 = R^3 = R^4 = Cl), 87-87-6; **2** (R^1 = R^2 = Cl, R^3 = R^4 = CN), 4640-41-9; **2** (R^1, R^2 = CH=CH—CH=CH, R^3 = R^4 = H), 571-60-8; **3a**, 70524-44-6; **3b**, 70524-45-7; **3c**, 70524-46-8; **3d**, 70524-47-9; **3e**, 70562-41-3; **4a**, 70524-48-0; **4b**, 70524-49-1; **4c**, 70524-50-4; **4d**, 70524-51-5; **4e**, 70562-40-2; **5**, 70524-52-6; **6**, 70524-53-7; **7**, 5803-27-0; **8**, 70524-54-8; **9a**, 53554-47-5; **9b**, 56625-59-3; **9c**, 53554-48-6; **10a**, 54393-49-6; **10b**, 56625-60-6; **10c**, 56594-64-0; **11a**, 3750-47-8; **11b**, 56594-65-1; **11c**, 56594-66-2; **12a**, 54393-52-1; **12b**, 56594-67-3; **12c**, 56594-68-4; **14a**, 70524-56-0; **14b**, 70524-57-1; **14c**, 70524-58-2; **14d**, 70524-59-3; **14e**, 70524-60-6; **14f**, 70524-61-7; **15**, 70524-62-8; *N*,*N*-diethylhydroxylamine, 3710-84-7; 3-(4-nitrophenoxy)propanesulfonyl chloride, 61387-38-0; benzenesulfonyl chloride, 98-09-9; *p*-methylbenzenesulfonyl chloride, 98-59-9; *p*-chlorobenzenesulfonyl chloride, 98-60-2; *p*-acetamidobenzenesulfonyl chloride, 121-60-8; 4-isopropoxy-1-naphthol, 41426-37-3; 4-(2-methoxyethoxy)-1-naphthol, 70524-63-9; 4-(2-ethoxyethoxy)-1-naphthol, 53554-58-8.