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Novel Oxidative Dye Couplers

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ABSTRACT

*We have evaluated novel oxidative dye couplers based on 4,6-bis(aryloxy)-*m*-phenylenediamines. The aryloxy groups are displaced upon coupling and then participate in further color formation. A mixture of up to four different dyes can therefore be produced from a single coupler–primary intermediate interaction.*

INTRODUCTION

While the convenience and general quality of permanent hair coloring products has improved over the past few decades, the chemistry has essentially remained unchanged. Current commercial products continue to rely for color formation on the hydrogen peroxide-induced oxidative coupling between low-molecular-weight primary intermediates (commonly *para*-substituted benzenes) and color modifiers (commonly *meta*-substituted benzenes). Each couple produces a specific color: shades are then formulated from suitable mixtures of the various components. Formulas therefore contain a significant number of dye precursors in order to produce natural-looking shades and the associated chemistry involves a complex series of competing reactions. This paper describes a hair coloring system which requires considerably fewer components and yet produces the same dyes and shades as current products.

Recent work has shown that couplers with alkoxy groups *para* to the amino or hydroxy functions undergo coupling with elimination of the

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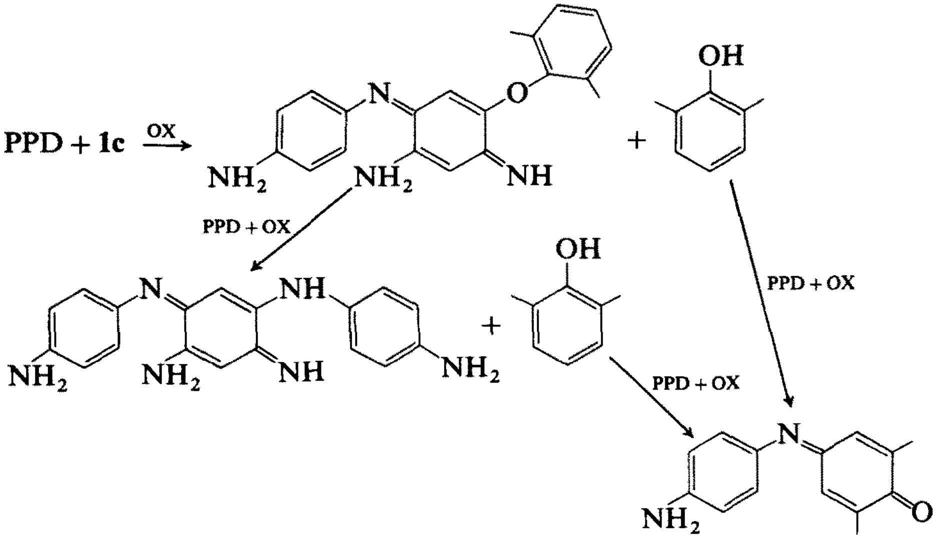

Scheme 1. Oxidative dye formation from coupler **1c** and excess *p*-phenylenediamine (PPD).

alkoxys.[1] In fact, couplers such as 4,6-dialkoxy-*m*-phenylenediamines appear to be superior to the more commonly used 4-alkoxy-*m*-diamines.[2] We have now evaluated similar couplers with 4,6-diaryloxy groups with a view to exploiting the liberated aryloxy (phenoxy) groups in further color-forming reactions (Scheme 1). Careful selection of the aryl group would then allow for a significant reduction in the total number of components in the overall coloring system since a single coupler of this type can replace up to three of the conventional couplers.

EXPERIMENTAL

Commercially available reagents were used wherever possible without purification. The couplers were prepared from *m*-dichlorobenzene by dinitration at the 4- and 6-positions followed by substitution of the halogens by phenolate and reduction of the nitro groups.

2,4-Dinitro-1,5-dichlorobenzene

To a mixture of 150 ml of fuming nitric acid and 150 ml conc. sulfuric acid cooled to 10–15°C was added 100 ml (128·8 g; 0·88 mol) *m*-dichlorobenzene over 1 h. External cooling was used to maintain the temperature during the addition, then the mixture was allowed to equilibrate to room temperature. The mixture was then heated to 80°C for about 2 h until TLC (hexanes) showed total loss of starting material. After cooling, the yellow precipitate was filtered and washed free of residual acid. Yield 232·3 g (98%), m.p. 98–100°C.

4,6-Diphenoxy-1,3-dinitrobenzene

Under argon, 24·4 g (0·25 mol) of phenol and 250 ml toluene were added to a solution of 9·6 g (0·24 mol) NaOH in 25 ml water with stirring. The water was azeotropically distilled off with the toluene and, after cooling, 23·7 g (0·1 mol) of the dinitrodichlorobenzene was added. After reflux for 2 h, TLC (toluene) showed a single product. The solution was filtered hot, cooled and refiltered to give a pale yellow solid (18·5 g, 53%), m.p. 129°C. Found: C, 61·2; H, 3·6; N, 7·9; O, 27·0. Calc. for $C_{18}H_{12}N_2O_6$: C, 61·4; H, 3·4; N, 8·0; O, 27·3%. Mass spectrum: *m/e* 352, 259, 213, 183, 171.

4,6-Diphenoxy-1,3-diaminobenzene dihydrochloride (1a)

The dinitro compound (2 g) was suspended in 75 ml ethanol and 0·01 g of 10% Pt/C catalyst was added. Reduction was carried out on a Parr hydrogenator at 50°C and 50 psig hydrogen. After complete reaction, the mixture was filtered into 400 ml of ethyl acetate saturated with HCl gas. The solvent was removed under vacuum until a pale tan solid precipitated (2·05 g, 90%). Mass spectrum: *m/e* 292, 215, 198, 187, 149. NMR: δ 6·3 (1 H, s); 7·0–7·3 (11 H, m).

Other couplers

The following compounds were prepared similarly:

4,6-bis(2-methylphenoxy)-1,3-diaminobenzene dihydrochloride (**1b**);
4,6-bis(2,6-dimethylphenoxy)-1,3-diaminobenzene dihydrochloride (**1c**);
4,6-bis(1-naphthyloxy)-1,3-diaminobenzene dihydrochloride (**1d**);
4,6-bis(2-methyl-5-aminophenoxy)-1,3-diaminobenzene tetrahydrochloride (**1e**);
4,6-bis(2,4-dimethylphenoxy)-1,3-diaminobenzene dihydrochloride (**1f**).

For coupler **1e** where the aryloxy substituent carries an amino group, substitution was effected with the corresponding nitrophenolate and the nitro group was reduced in the final synthetic step. The high-melting hydrochloride salts were difficult to characterize so product identification was assured at the di- or tetra-nitro stage. All gave satisfactory data as follows.

4,6-Bis(2-methylphenoxy)-1,3-dinitrobenzene
M.p. 119–120°C. Found: C, 63·2; H, 4·3; N, 7·1; O, 25·0. Calc. for $C_{20}H_{16}N_2O_6$: C, 63·2; H, 4·2; N, 7·4; O, 25·3%. Mass spectrum: *m/e* 380, 363, 288, 273, 227, 197.

4,6-Bis(2,6-dimethylphenoxy)-1,3-dinitrobenzene
M.p. 208°C. Found: C, 64·7; H, 5·0; N, 6·8; O, 23·4. Calc. for $C_{22}H_{20}N_2O_6$: C, 64·7; H, 4·9; N, 6·9; O, 23·5%. Mass spectrum: *m/e* 408, 377, 349, 330, 311, 288.

4,6-Bis(1-naphthyloxy)-1,3-dinitrobenzene
M.p. 135–137°C. Found: C, 69·0; H, 3·9; N, 5·9; O, 21·2. Calc. for $C_{26}H_{16}N_2O_6$: C, 69·0; H, 3·5; N, 6·2; O, 21·2%. Mass spectrum: *m/e* 452, 358, 329, 285, 263, 233.

4,6-Bis(2-methyl-5-nitrophenoxy)-1,3-dinitrobenzene
M.p. 171–173°C. Found: C, 51·8; H, 3·1; N, 11·3; O, 33·2. Calc. for $C_{20}H_{14}N_4O_{10}$: C, 51·1; H, 3·0; N, 11·9; O, 34·0%. Mass spectrum: *m/e* 470, 424, 380, 318, 271, 242. NMR: δ 2·3 (6H, s); 6·7 (1H, s); 7·6–8·0 (6H, m); 9·0 (1 H, s).

4,6-Bis(2,4-dimethylphenoxy)-1,3-dinitrobenzene
M.p. 148°C. Found: C, 64·5; H, 5·0; N, 6·7; O, 23·5. Calc. for $C_{22}H_{20}N_2O_6$: C, 64·7; H, 4·9; N, 6·9; O, 23·5%. Mass spectrum: *m/e* 408, 375, 344, 314, 288, 271, 241, 211.

Hair dyeing

Swatches (2 g) were prepared from blended gray or commercially bleached hair from DeMeo Brothers, New York, USA. Dye baths (4 g) contained 1% by weight of the coupler in 35% aqueous ethanol, the appropriate amount (2, 3 or 4 molar equivalents) of the primary intermediate, and 3% hydrogen peroxide as oxidant, adjusted to pH 10 with ammonium hydroxide. The hair was soaked in the dye mixture for 20 min, rinsed under running tap-water and dried. Color was assessed visually and by Hunter Tristimulus readings.

RESULTS AND DISCUSSION

Colors produced in solution and on hair[3] from *p*-phenylenediamine (PPD) and appropriate couplers are shown in Table 1. In general, the *m*-diamine couplers will give a violet color on hair, phenolic couplers will add significant

TABLE 1
Colors from Oxidation Dye Couplers and *p*-Phenylenediamine

Coupler	λ_{max} (H_2O) (*nm*)	*Hair color*
Phenol	554	Blue
2-Methylphenol	537	Blue
2,6-Dimethylphenol	525	Violet/blue
1-Naphthol	523	Violet/blue
6-Methyl-3-aminophenol	492	Red/magenta
4-Methoxy-*m*-phenylenediamine	520[a]	Violet

[a] Broad band 510–535 nm.

blue and the aminophenols will add red. However, in a preliminary test using coupler **1a**, no increase in the blue (Hunter negative *b* values) shading was observed as the molar excess of PPD was increased. This initially surprising result can be explained by considering values of published rate constants for the various color-forming reactions.

In this analysis we will consider only coupling reactions with *p*-benzoquinonedi-imine, the initial oxidation product of PPD, although a similar process can be used for all other primary intermediates. It has been shown[3] that all commercially useful couplers have coupling rate constants (k) with PPD of approximately 10^5 litre mol^{-1} min^{-1} at pH 9–10. Therefore, couplers such as phenol ($k = 2 \times 10^3$ litre mol^{-1} min^{-1})[4] are not sufficiently reactive to compete with other couplers present in the mixture. In contrast, 2,6-dimethylphenol ($k = 2 \times 10^5$ litre mol^{-1} min^{-1})[4] and 1-naphthol ($k = 1 \times 10^6$ litre mol^{-1} min^{-1})[4] are reactive enough to compete. In the above experiment, therefore, even though phenolate may be liberated on coupling, it is not sufficiently reactive to compete with unreacted **1a** for the di-imine and the dyed hair will only reflect the violet *m*-diamine color. (During oxidative hair dyeing there is a large excess of dye precursors and considerable amounts of unreacted couplers at any time. Therefore, the dye bath would never be depleted of **1a**.) However, Table 2 shows data from hair dyed with PPD and coupler **1c**. In this case, the dyed hair clearly shows the added blue color from the liberated and subsequently coupled phenolate as the PPD: **1c** ratio increases. Also included in this table are data from coupler **1b**, which gives an unreactive phenol, and from the 4,6-bis(2-hydroxyethyloxy)-*m*-phenylenediamine,[2] a commercially used coupler that cannot produce phenoxy fragments but is otherwise related to couplers **1**. In the latter two cases, within the experimental error, there is little change in shade (Hunter *a* and *b* values) as the PPD: coupler ratio increases. Under similar conditions **1c** shows a significant decrease in Hunter *b* (increase in

TABLE 2

Hunter Tristimulus Values for Gray Hair Dyed with PPD and 4,6-Di(R)-*m*-phenylenediamine with 3% H_2O_2 for 20 min at pH 10

	R								
	OCH_2CH_2OH			*2-Methylphenol*			*2,6-Dimethylphenol*		
Molar ratio, PPD/coupler	*L*	*a*	*b*	*L*	*a*	*b*	*L*	*a*	*b*
1:1	16·6	1·7	−2·2	23·2	1·5	2·6	11·1	1·7	2·7
2:1	13·8	1·4	−2·3	19·6	1·6	1·7	11·4	0·4	0·3
3:1	13·5	1·6	−2·1	19·5	1·8	2·0	9·4	2·7	−1·3
4:1	12·1	1·4	−2·1	20·0	2·0	3·0	11·7	2·5	−2·3

blue). As the PPD concentration increases, the dye color also appears to become more red (positive *a* value), which may be due to addition of PPD to the violet and blue indo dyes resulting in a drabbing effect (a process which commonly occurs during oxidative hair dyeing; see for example Ref. 3), or some self-coupling of PPD.

Under circumstances where an *m*-aminophenolate is released, e.g. **1e**, the hair color becomes more red and less blue on increasing the PPD-to-coupler ratio (Table 3). This table also shows the effects of a phenolate group that is unable to couple, **1f**, since the coupling (*para*) position is blocked with a methyl group. In this case, the shade changes little on adding more PPD. Coupler **1d** liberates a group which couples to give essentially the same color as the parent *m*-diamine. In this case, increase in the PPD/coupler ratio also produces only a small change in the hair color.

It is clear that 4,6-diaryloxy-*m*-phenylenediamines undergo oxidative dye formation with the displacement of, initially, one aryloxy group. This

TABLE 3

Hunter Tristimulus Values for Bleached Hair Dyed with PPD and Couplers **1d**, **1e** and **1f** with 3% H_2O_2 for 20 min at pH 10

Molar ratio, PPD/coupler	*Coupler*								
	1d			**1e**			**1f**		
	L	*a*	*b*	*L*	*a*	*b*	*L*	*a*	*b*
1:1	10·7	1·6	−4·4	—	—	—	25·2	2·3	0·3
2:1	9·7	0·6	−0·2	11·2	0·9	−0·9	17·4	1·9	−0·7
3:1	9·7	0·6	−0·2	9·6	2·2	−0·4	16·5	1·7	−0·2
4:1	9·3	−0·3	−0·2	—	—	—	14·6	2·0	−0·4

aryloxy group is then able, under most circumstances, to couple with the primary intermediate to produce a second dye. There is evidence to show that the initially formed dye can also react with additional primary intermediate to form a third dye with displacement of the remaining aryloxy group, which is then available for color formation. Thus, overall, one coupler molecule can react with up to four equivalents of primary intermediate, and produce three different dyes as shown in the reaction scheme. If the aryloxy groups are different, four distinct dyes would be produced. Thus it is possible to form the palette of colors commonly used in oxidative dye products from a single coupler and two or three primary intermediates.

A second use for such compounds involves protection of dye couplers which are usually decomposed by hydrogen peroxide: this includes some aminophenols and the yellow-forming 1,3-diketone derivatives. When chemically combined with an *m*-diamine coupler it appears that such compounds are unreactive towards the hydrogen peroxide in the dye bath. However, once displaced by the oxidative coupling reactions inside the hair, these couplers would be available for color formation. Thus, the large excesses of such compounds needed to overcome decomposition in the dyebath can be avoided.

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