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Oxidative Coupling of Aminonaphthols

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The oxidative coupling of three aminonaphthols by manganese(III) tris(acetylacetonate) was examined. The products from 5-amino-2-naphthol were enol-acetylacetonylidene-1-(6-hydroxynaphthyl)-imine (**1**) and 2,2′-dihydroxy-5,5′-diamino-1,1′-binaphthyl (**2**); those from 8-amino-2-naphthol were 4-(acetylacetone-3″-yl)-7,7′-dihydroxy-1,1′-azonaphthalene (**3**) and enol-acetylacetonylidene-7-hydroxy-1-naphthylimine (**4**); the product from 5-amino-1-naphthol was enol-acetylacetonylidene-4-hydroxy-1-naphthylimine (**5**).

We reported on the synthesis of a DOPA dimer[1] and Swan and Chapman reported on that of other DOPA dimers.[2] The compounds are of interest with respect to possible intermediacy of DOPA melanogenesis. Piattelli *et al.*[3] isolated several dimers of catechol from its oxidation products. The melanin precursor is very susceptible to oxidation making it difficult to regulate its oxidation to afford a specific dimer.

It is known that 2,3-dihydroxynaphthalene is dimerized into 2,2′,3,3′-tetrahydroxy-1,1′-binaphthyl by oxidative coupling using iron(III) alum,[4] and that 2,2′-dihydroxy-1,1′-binaphthyl is prepared by the oxidative coupling of 2-naphthol with manganese(III) tris(acetylacetonate).[5]

This suggests the possibility of controlling oxidation of phenolic compounds by selecting proper substrate, oxidant, solvent, and temperature. The results of investigation of the oxidative coupling of aminonaphthols are given. They are interesting as models of melanin precursors and also of practical importance as modification of hair dyes.[6]

Results and Discussion

Three available aminonaphthols were chosen as substrates. Oxidation was carried out under conditions suitable for oxidative coupling to give specific dimers. In order to do so, several known methods[5,7] recommended for the oxidative coupling of phenols were compared with the use of 2-naphthol as a reference. Manganese(III) tris(acetylacetonate) (MTA) shows the best result (Table 1).

TABLE 1. OXIDATION PRODUCTS FROM 2-NAPHTHOL AND 5-AMINO-2-NAPHTHOL WITH SEVERAL OXIDANTS

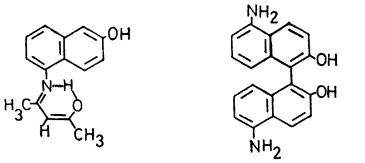
Oxidant	Oxidation products			
	(2-Naphthol)		(5-Amino-2-naphthol)	
	Dimer	Polyer*	Dimer	Polymer[a)]
O_2/OH^- [8]	+	+	−	++
$K_3Fe(CN)_6$[9,10]	+	+	−	++
$FeCl_2$[11]	+	+	−	++
$VOCl_3$[7]	++	−	−	+
MTA[5]	++	−	++	−

a) Polymer: The products were black tar and did not dissolve in any solvents.

1) Y. Omote, Y. Fujinuma, and N. Sugiyama, *Chem. Commun.*, **1968**, 190; This Bulletin, **42**, 1752 (1969).
2) R. F. Chapman, G. A. Swan, *J. Chem. Soc., C*, **1970**, 865.
3) M. Piattelli, E. Fattorusso, R. A. Nicolaus, and S. Magno, *Tetrahedron*, **21**, 3229 (1965).
4) H.-W. Wanzlick, M. Lehmann-Horchler, and S. Mohrmann, *Chem. Ber.*, **90**, 2529 (1957).
5) M. J. S. Dewar and T. Nakaya, *J. Amer. Chem. Soc.*, **90**, 7134 (1968).
6) a) H. H. Tucker, *J. Soc. Cosmetic Chem.*, **18**, 608 (1967); H. H. Tucker and I. Schwartz, *ibid.*, **22**, 139 (1971). b) E. Tsuchida, M. Kaneko, and Y. Kurimura, *Makromol. Chem.*, **132**, 209 (1970).
7) W. L. Carrick, G. L. Karapinka, and G. T. Kwiatkowski, *J. Org. Chem.*, **34**, 2388 (1969).
8) H. Musso and C. Rathjen, *Chem. Ber.*, **96**, 1563 (1963).
9) R. J. Molyneux, A. C. Waiss, Jr., and W. F. Haddon, *Tetrahedron*, **26**, 1409 (1970).
10) C. G. Haynes, A. H. Turner, and W. A. Waters, *J. Chem. Soc.*, **1956**, 2823.
11) D. R. Nelan and C. D. Robeson, *J. Amer. Chem. Soc.*, **84**, 2963 (1962).

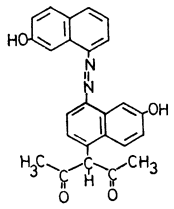
Aminonaphthols were oxidized with MTA in acetonitrile at 80°C under nitrogen atmosphere. From 5-amino-2-naphthol two products were obtained. One product with R_f 0.39 and mp 185°C was proved to have the structure **1** because the NMR spectrum in $CDCl_3$ of the substance showed the peaks at δ 2.15 (s, methyl 3H), 5.3 (s, methine 1H), 7.1—7.9 (m, naphthalene 6H), 9.9 (broad, phenolic 1H, disappeared with D_2O), and 12.8 (s, enol 1H, disappeared with D_2O). Both elemental analyses and mass spectrum also fit the structure **1**. The other product with R_f 0.17 and mp 230°C showed the peaks at δ 3.0 (s, aromatic amine 4H), 5.05 (broad s, phenolic 2H) and 6.3—8.0 (m, naphthalene 10H) in the NMR spectrum in acetone-d_6. This revealed the structure **2**, which was also supported by elemental analyses and mass spectrum.

In case of the oxidative coupling of 6-amino-2-naphthol, binaphthyl-type dimer was not obtained, but a 1,1′-azonaphthalene-type dimer (**3**) was obtained accompanied by enol-acetylacetonylidene-hydroxynaphthylimine (**4**). The structure **3** is in accord with the NMR spectrum in $CDCl_3$ which showed the peaks at δ 1.75 (two s, two methyl 6H), 1.7 (broad, phenolic 2H, disappeared with D_2O), 3.2 (s, methine 1H), and 6.2—7.8 (m, naphthalene 11H).



1

2



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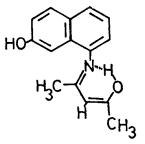

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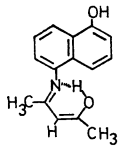
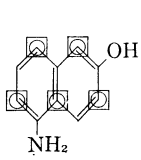
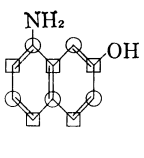
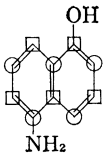


5

The UV spectrum of **3** also supports azonaphthalene structure showing λ_{max}(EtOH) at 255, 262 (sh), 315, 390, 409, and 514 nm. Recently Stead[12] reported on the formation of 2,8,8′-trihydroxy-1,1′-azonaphthalene-3,6,3′,6′-tetrasulfonic acid from the coupling of diazotized 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid. It is interesting that a similar 1,1′-azonaphthalene is directly obtained by the oxidative coupling of an aminonaphthol.

The oxidative coupling of 5-amino-1-naphthol gave neither C–C coupling product like **2**, nor N–N coupling product like **3**, but afforded C–N coupling product between 5-amino-1-naphthol and acetylacetone from MTA. The structure of C–N coupling product is proposed as **5**. Spectral proofs of structure **4** and **5** are as follows. The NMR spectrum in $CDCl_3$ of **4** showed signals at δ 1.85 (s, 3H), 2.15 (s, 3H), 2.70 (broad, 1H), 5.30 (s, 1H), 7.10—7.90 (m, 6H), and 12.5 (s, 1H), and that of **5** showed signals at δ 1.9 (s, 3H), 2.2 (s, 3H), 5.3 (s, 1H), 6.9—7.5 (m, 6H), 9.1 (broad, 1H), and 12.6 (s, 1H).

Table 2. Linking of oxidative coupling of aminonaphthols

Coupling			
C–C	+ (**2**)	—	—
N–N	—	+ (**3**)	—
C–N	+ (**1**)	+ (**4**)	+ (**5**)

The mark (○) shows a position which will be radical rich by resonance when naphthoxy radical is formed. The mark (□) shows a position where electron density is large because of the electron releasing effect of amino group. The mark (+) means positive reaction and the product is shown by a number in ( ).

The results of the oxidative coupling of three aminonaphthols are summarized in Table 2. In the case of 5-amino-2-naphthol, the C–C coupling is possible because the inductive effect of amino group will increase radical density at *ortho* position to hydroxyl group. In the case of 8-amino-2-naphthol, however, the C–C coupling at *ortho* position is prevented by steric hindrance of amino group, affording the N–N coupling product. In the case of 5-amino-1-naphthol, *ortho* position to hydroxyl group is not active enough to dimerize, only the C–N coupling product being obtained. The C–N coupling product between amino group and acetylacetone of MTA is formed in every case.[13]

Experimental

Enol-acetylacetonylidene-1-(6-hydroxynaphthyl)imine (1). 5-Amino-2-naphthol (0.79 g) was added to a solution of acetonitrile (30 ml) containing manganese(III) tris(acetylacetonate) (MTA) (2.11 g) under atmosphere of nitrogen. The mixture was stirred and kept under reflux at 80°C overnight. The solvent was then evaporated under reduced pressure. The concentrated product was examined by tlc (silica gel, benzene–ethyl acetate, 2: 1, v/v), two spots being observed at R_f 0.39 and 0.17. A portion (0.5 g) of the crude product was purified by silica gel column chromatography using the mixture of benzene and ethyl acetate (2: 1, v/v). The first fraction having R_f 0.39 gave a pale yellow solid which was recrystallized from benzene–ethyl acetate as pale yellow needles, mp 185°C (0.16 g). IR (KBr): 3100, 2900, 1630, 1600, 1500, 1430, 1420, 1300, and 900 cm^{-1}. MS (*m/e*): 241 (M^+).

12) C. V. Stead, *J. Chem. Soc., C*, **1970**, 693.

13) K. Kaeriyama, This Bulletin, **43**, 1511 (1970).

Found: C, 74.71; H, 6.23; N, 5.84%. Calcd for $C_{15}H_{15}O_2N$: C, 74.66; H, 6.27; N, 5.81%.

2,2'-Dihydroxy-5,5'-diamino-1,1'-binaphthyl (2). Evaporation of the second chromatographic fraction of the preceding experiment gave a gray solid which was reprecipitated from benzene–ethyl acetate to give grayish powder (0.2 g), mp 230°C (decomp.).

IR: (KBr) 3370, 3300, 1620, 1590, 1510, 1429, 930, and 810 cm^{-1}. MS (*m/e*): 316 (M^+).

Found: C, 75.73; H, 5.36; N, 8.88%. Calcd for $C_{20}H_{16}O_2N_2$: C, 75.93; H, 5.10; N, 8.86%.

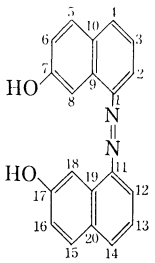
4-(Acetylacetone-3"-yl)-7,7'-dihydroxy-1,1'-azonaphthalene (3). A mixture of 8-amino-2-naphthol (0.8 g), acetonitrile (40 m*l*) and MTA (2.1 g) was treated in the same way as described above. The first elution of column chromatography gave red powder (0.21 g) which was reprecipitated from benzene, mp 251—252°C (decomp.). IR (KBr): 3400, 2900, 1705, 1685, 1655, 1625, 1590, 1320, and 830 cm^{-1}.

Found: C, 73.20; H, 4.94; N, 6.88%. Calcd for $C_{25}H_{20}O_4N_2$: C, 72.80; H, 4.89; N, 6.79%.

Enol-acetylacetonylidene-7-hydroxy-1-naphthylimine (4). The second fraction of the preceding chromatography gave a pale yellow solid which was recrystallized from benzene–ethyl acetate as pale yellow needles (0.04 g), mp 179—180°C. IR (KBr): 3400, 3100, 2900, 1620, 1600, 1550, 1320, 1250, and 1220 cm^{-1}.

Enol-acetylacetonylidene-4-hydroxy-1-naphthylimine (5). A mixture of 5-amino-1-naphthol (0.8 g), acetonitrile (40 m*l*) and MTA (2.5 g) was treated in the same way as described above. Only one product could be obtained. It was purified by column chromatography and recrystallization from ethyl acetate to give pale yellow needles (0.14 g), mp 187—188°C. IR (KBr): 3000, 2800, 1625, 1600, 1550, 1420, 1380, and 820 cm^{-1}. MS (*m/e*): 241 (M^+).

Calculation of S_R of 7,7'-Dihydroxyazonaphthalene. In order to determine the position of acetylacetonyl group in compound **3**, it was assumed that **3** was formed by the reaction of 7,7'-dihydroxyazonaphthalene radical and MTA. Parameters and superdelocalizability (radical) were as follows.



$$\alpha_{\dot{N}} = \alpha + 0.5\beta$$

$$\alpha_{\dot{O}} = \alpha + 2.0\beta$$

$$\beta_{NC} = 0.8\beta$$

$$\beta_{OC} = 0.8\beta$$

$$\beta_{NN} = 1.0\beta$$

Position No.	S_R(R)	Position No.	S_R(R)
1	0.9087	6	0.8887
2	1.0925	7	0.8859
3	0.8684	8	1.0129
4	1.1790	9	0.7690
5	1.0282	10	0.7129

The value of S_R(R) shows that position No. 4 will be most active in radical reaction.

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