Reactions of 2-Amino-1,4-Naphthoquinone with Aldehydes.

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Abstract: reactions between 2-amino-1,4-naphthoquinone with aldehyeds give 2-(N-alkenyl) amino-1,4-naphthoquinone (**7**) under neutral conditions while they give substituted 1H-2,4-dihydronaphtho[2,3-d]1,3-oxazine-5,10-diones (**8**) using catalytic amount of triflouroacetic acid.

Keywords: aldehydes; amines; quinones; alkylation

Introduction:

The reactions of 2-amino-1,4-naphthoquinone as nucleophiles have received little attention due to the poor nucleophilicity of the amino group which is considered to have an "amide like" character.[1,2] For instance, intramolecular **N**-acylation of some aminoquinones has required their prior reduction to the more basic amino-naphthohydroquinone derivatives.[3,4] Lately, 2-amino-1,4-naphthoquinone has been shown to have some reactivity with some electrophiles such as β-dielectophiles,[2] methyleniminium salts.[5] In these reactions , the N-alkylation was found to be the principal product. We wish to report here, the reactions of 2-amino-1,4-naphthoquinone with aldehydes and the conditions that lead to **N** versus **C** alkylations.

Results and Discussion

Scheme 1 shows that 2-amino-1,4-naphthoquinone, **1**, is in resonance with structure **2** . Therefore, there are two nucleophilic sites present in the molecule, **N** of the amino group and C-3. Both **1** and **2** can direct an incoming electrophile to their nucleophilic sites and thus, can lead to the corresponding alkylated products **3** and **4,** respectively.

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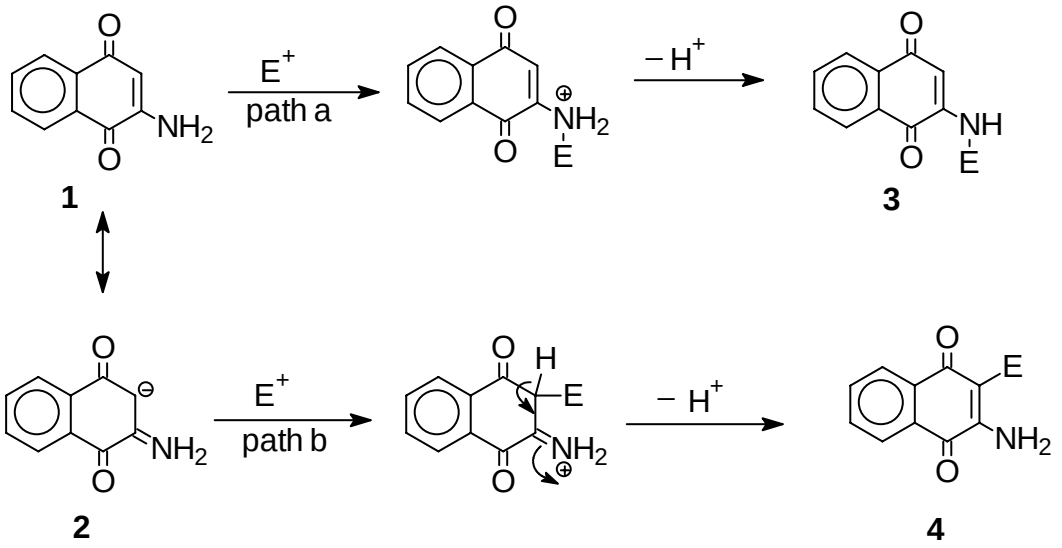
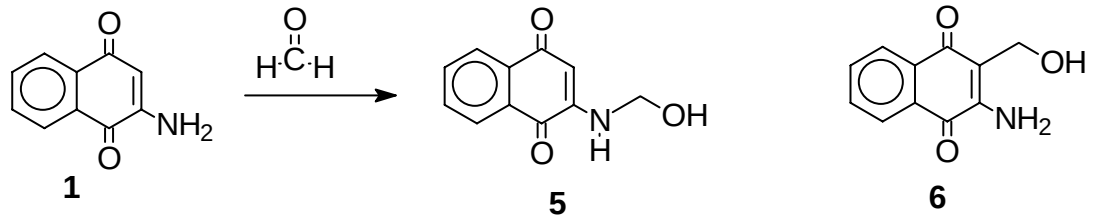


Scheme 1

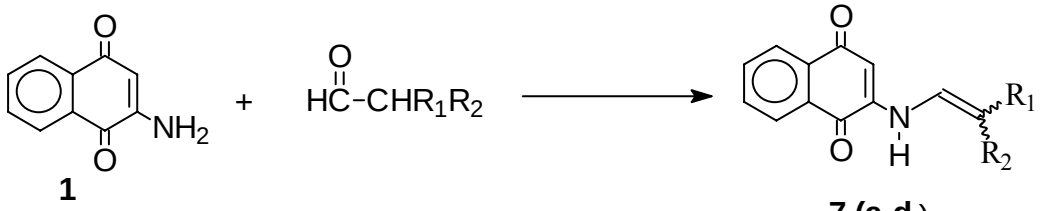
The following examples illustrate the above reaction scheme. Formaldehyde reacts with aminoquinone **1** in $CHCl_3$ at room temperature and gives exclusively **N**-(hydroxymethyl) aminoquinone **5** in 64% yield(Scheme 2). There is no observed product corresponding to nucleophilic substitution at C-3 (compound **6**). This means that **1** did not act as enamine compound and the reaction followed path "a" in scheme 1.



Scheme 2

Mőhrle and Herbrűggen[5] have shown that aminoquinone **1** , reacts with methyliminium salts to give **N**-aminomethyl compound,**3**, under kinetic control. Compound **3** subsequently generates the thermodynamically stable C- Mannich product **4**. We have not observed such equilibration. Product **5** is found to be stable under neutral conditions even after refluxing it in $CHCl_3$ for 2 days and product **6** was not observed.

In a similar fashion, aminoquinone **1**, reacts with other aldehydes under neutral conditions to give **N**-(alkenyl) aminoquinones **7**a-d in 47-56 % yield (scheme 3). The reaction followed path "a" mechanism (scheme 1) to produce **N** alkylated products which on subsequent elimination of water afforded **7**. Dean Stark apparatus was used in these experiments in order to remove water and drive the reaction to completion. It is expected that product 7 (a-c) can exist as an E or a Z isomer. This expectation is confirmed by proton NMR, which showed that product 7(a-c) is a mixture of these isomers. The ratio of the E : Z isomers is determined by the olefinic protons coupling constant ;14 Hz for the E isomer and 7 Hz for the Z isomer. Scheme 2 shows that the E isomer predominates.

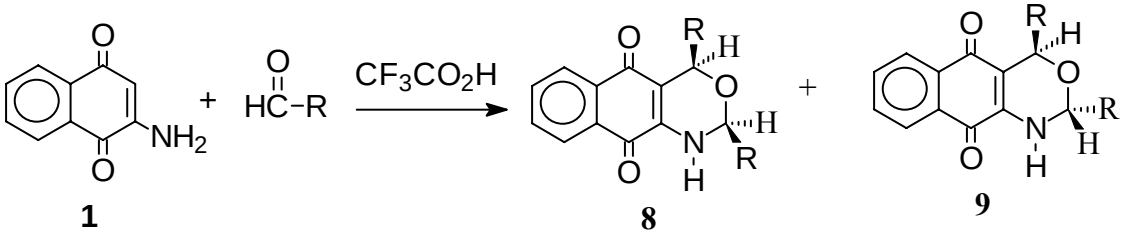


1 **7 (a-d)**

compond	R_1	R_2	% Yield	E : Z ratio
7a	H	C_2H_5	47	88 : 12
7b	H	C_3H_7	49	90 : 10
7c	H	C_4H_9	50	95 : 5
7d	CH_3	CH_3	56	--------

Scheme 3

On the other hand, using catalytic amount of triflouroacetic acid, aminoquinone**1** reacts with aldehydes at room temperature to produce substituted 1H-2,4-dihydronaphtho[2,3-d]1,3-oxazine-5,10-diones **8** and **9** in 54-70 % yield (scheme 4). Except for diastereomers **8e** and **9e**, which were separated by flash chromatography , all other **8** and **9** diastereomers were inseparable . The ratio of the cis (**8**) to trans (**9**) isomers in each of the mixture was determined by integration of the non-overlapping peaks in the proton NMR spectra. The reaction is stereospecific ; the cis stereoisomer is the predominant isomer in each case.



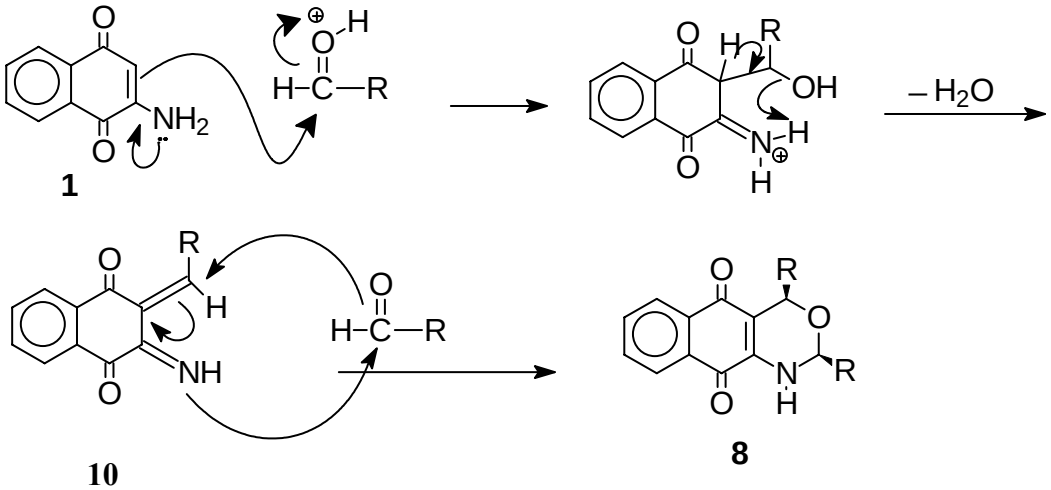
1 **8** **9**

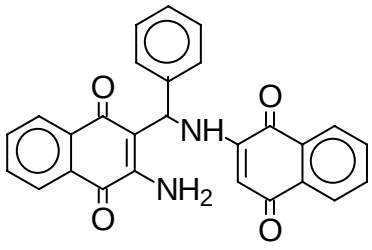
compound	**R**	**% Yield**	**8:9**
a	H	66	----
b	CH_3	67	90:10
c	C_2H_5	70	96:4
d	n-C_3H_7	64	94:6
e	i-C_3H_7	54	74:26
f	C_4H_9	57	89 :11

Scheme 4

The stereochemical assignment of **8b** was determined by NOE experiment and corroborated the finding of Marcos et al[6]. Thus, irradiation of **8b** at H-2 signal (5.10 ppm) in a NOE difference Experiment produced significant enhancement at H-4(5.03 ppm) and NH(5.88 ppm) protons resonances. Marcos et al[6] obtained compound **8**b at a lower yield (36 %) using 1,1-diethoxyethane instead of acetaldehyde. Under our experimental conditions that the reaction is general for aldehydes and produces the heterocyclic product in good yield.

A plausible reaction mechanism for the formation of compound **8** involves **C**-3 alkylation (path "b" scheme 1) followed by water elimination to produce the azadiene intermediate **10**(scheme 5). This intermediate is reactive enough to produce the cyclized product **8** by trapping another aldehyde molecule most likely by Diels-Alder reaction. A precedence for this type of cycloaddition is found in reaction of 2-hydroxy-1,4-naphthoquinone with citronelal [7]. Evidence in support of the formation of the intermediate **10** is the isolation of compound **11** in 24 % yield when benzaldehyde is allowed to react with aminoquinone **1**. Compound **11** must have been formed through the attack of intermediate **10** by another molecule of aminoquinone.





11

Scheme 5

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In conclusion, the reaction of aminonaphthoquinone **1**, with aldehydes produces the N-alkylated product under neutral conditions and the C-3 alkylated product under acidic conditions. The reaction, under acidic conditions , may first proceed by N-alkylation (kinetically controlled product) then equilibrate to the thermodynamically stable product . This work broaden the application of 2-amino-1,4-naphthoquinone in organic synthesis. The method provides a new synthetic route to heterocyclic quinones in one pot reaction in good yield. The scope of reactions of aminoquinone with other electrophiles is under current investigation.

EXPERIMENTAL:

All melting points are uncorrected. IR spectra were recorded on Nicolet 5 DBX FT IR and are reported in wave numbers(cm^{-1}). The NMR spectra were recorded on Joel Lambda 500 MHz NMR spectrometer, using deuterchloroform as a solvent unless otherwise noted. Mass spectra at 70 ev E.I. were recorded on the JEOL HX100 triple sector (EBE) high resolution mass spectrometer. Elemental analyses were performed on a Fisons 1108 Elemental analyzer. Chromatographic separations were performed using flash column and silica gel-60. All solvents were reagent grade.

2-(N-hydroxymethyl) amino-1,4-naphthoquinone 5 .

In 125 ml Erlenmeyer flask , 200 mg (1.15 mmol)of aminoquinone **1** and 5ml of 38% formaldehyde solution with 50 ml chloroform were added. The flask was stoppered and the mixture was stirred at room temperature for 3 days. The solvent was evaporated and the residue was recrystallized from CH_3OH to produce 150 mg (64% yield) of light red solid **5** . mp. 228-230. IR (KBr) 4470(s),3362(s),1683(m),1608(s),1568(s),and1022(s) cm^{-1}; $\delta_H(CD_3OD)$ 4.80(s,2H), 6.00(s,1H), 7.79(m,1H), 7.88(m,1H),8.85(m,2H).Anal. Calcd.for $C_{11}H_9NO_3$: C,65.02; H,4.46; N,6.89; Found: C, 64.93;H, 4.39; N, 6.62.

General procedure for preparing 2-(N-alkenyl) amino-1,4-naphthoquinone 7:

In 100ml round bottom flask fitted with Dean Stark apparatus and a reflux condenser, 50 ml of benzene along with 250mg (1.45 mmol) of aminoquinone, **1** ,and 2 ml (excess) of the aldehyde were added. The reaction mixture was refluxed for 5 days. The solvent was removed and the residue was chromatographed on silica-gel using dichloromethane as eluant. The product was recrestallized from ether-hexane mixture to yield a dark red needle crystals.

2-(N-1-propenyl)amino-1,4-naphthoquinone 7a (E and Z isomers):

Yield (145mg, 47%), m.p. 149-151. IR(KBr): 3250(m),1678(s),1602(s),1566(s),1502(s),1344(m),and1276(m) cm^{-1}. ^{1}HNMR $\delta_H(CDCl_3)$for the E isomer:1.70(dd,J_1=7.0Hz,J_2=1.45Hz,3H), 5.37(two overlapped quartets, J_1=7Hz, J_2=14Hz ,1H), 5.88(s,1H), 6.20(m,1H), 7.35(br,NH), 7.52(m,1H),7.63(m,1H),7.95(m,1H); Non-overlapping peaks for the minor Z isomer were present at 5.02(pentet,1H). The ratio of the E and Z isomers was

determined to be 88: 12 respectively, by integration. Anal. Calcd. For $C_{13}H_{11}NO_2$: C,69.83; H,5.86; N,7.40. Found: C,69.64; H,5.72; N,7.32.

2-(N-1-butenyl)amino-1,4-naphthoquinone 7b(E and Z isomers):

Yield(160mg, 49 %), mp. 155-157. IR(KBr): 3210(m),3157(m),2963(m),1680(m),1603(s),1571(s),1509(s),and 1275(m)cm^{-1}. ^{1}HNMR $\delta_H(CDCl_3)$for the E isomer: 1.04(t,J=7.4Hz,3H),2.13(pentet of doublet, J_1=7Hz, J_2=1.5Hz,2H),5.48(td,J_1=14 Hz, J_2=7Hz,1H),5.95(s,1H),6.26(m,1H),7.37(br,NH),7.61(td,J_1= 7.5Hz, J_2=1.3Hz,1H),7.72(td,J_1= 7.5Hz, J_2=1.3Hz,1H),8.03(dd,J_1= 7.5Hz, J_2=1.1Hz,1H),8.08(dd,J_1= 7.5Hz, J_2=1.1Hz,1H). Non-overlapping peaks for the minor Z isomer were present at 1.08(t,J=7.5Hz,3H),2.19(pentet of doublet,J_1= 7.5Hz, J_2=1.5Hz,1H), 5.01(q, J=7.5Hz, 1H),6.18(m,1H),7.34(br,NH). The ratio of the E and Z isomers was determined to be 90: 10 respectively, by integration. C-13NMR $\delta(CDCl_3)$: 13.83,23.28,102.01,119.91, 121.82,126.21,126.38, 130.29,132.22, 133.40, 134.85,143.15,181.73,182.98. m/z: 227(M^+,100%). Anal. Calcd. For $C_{14}H_{13}NO_2$: C,73.99;H,5.77; N,6.16. Found; C,73.87; H,5.49; N,5.98.

2-(N-1-pentenyl)amino-1,4-naphthoquinone 7c (E and Z isomers):

Yield (175 mg, 50.3%).mp.152-154. IR(KBr): 32.12(m),1602(s),1568(s),1506(m),1348(m),and 1276(s) cm^{-1}. ^{1}HNMR $\delta_H(CDCl_3)$for the E isomer: 0.92(t,J=7.4Hz,3H),1.43(sixtet,J=7.4Hz, 2H), 2.07(dq,J_1=7Hz, J_2=1.3Hz,2H), 5.44(dt,J_1=14 Hz, J_2=7Hz, 1H), 5.95(s,1H), 6.26(m,1H), 7.37(br,1H),7.60(dt, J_1=7.5Hz,J_2=1.3Hz,1H),7.71(dt, J_1=7.5Hz, J_2=1.3Hz,1H), 8.04(dd, J_1=7.5Hz,J_2=1.2Hz,1H),8.08(dd, , J_1=7.5Hz,J_2=1.2Hz,1H). Non-overlapping peaks for the minor Z isomer were present at 0.96(t,J=7.4Hz,3H),1.49(sixtet,J=7.4Hz,2H), 2.15(dq,J_1= 7.5Hz, J_2=1.7Hz,2H), 5.02(q, J=7.5Hz, 1H),5.95(s,1H),6.17(m,1H),7.35(br,NH). The ratio of the E and Z isomers was determined to be 95: 5 respectively, by integration. C-13 NMR $\delta(CDCl_3)$: 13.56,22.86,32.12,102.02, 118.15, 122.57, 126.22, 126.40, 130.29, 132.11,133.49,134.85,143.10,181.69,182.84. Anal. Calcd for $C_{15}H_{15}NO_2$: C,74.67; H,6.27; N,5.80. Found: C,74.52; H,6.14; N,5.67.

2-(N-2-methyl-1-propenyl)amino-1,4-naphthoquinone 7d :

Yield (185 mg, 56%); mp.156-157. IR(KBr): 3280(m),2932(m),1674(m),1608(s),1566(m), and1490(s) cm^{-1}. ^{1}HNMR $\delta_H(CDCl_3)$: 1.79(d,J=0.9Hz,3H), 1.82(s,3H), 5.92(s,1H), 6.06(m,1H), 7.30(br, NH), 7.63(dt, J_1=7.5Hz,J_2=1.3Hz,1H),7.74(dt, , J_1=7.5Hz,J_2=1.3Hz,1H), 8.07(m,1H),8.10(m,1H). Anal. Calcd for $C_{14}H_{12}NO_2$: C,74.32; H,5.35; N,6.19. Found: C, 74.31; H, 5.40; N, 5.97.

General procedure for preparing 2,4-dialkyl-1H-2,4-dihydronaphtho[2,3-d]1,3-oxazine-5,10-diones (8) and 9: To a solution of aminoquinone **1** (250mg, 1.45 mmol) and 1 ml (excess) of the appropriate aldehyde in 50 ml of chloroform, triflouroacetic acid(3 drops) was added. The reaction mixture was stirred at room temperature for few days. Then , the solvent was removed and the residue was recrystallized from CH_3OH.

1H-2,4-dihydronaphtho[2,3-d]1,3-oxazine-5,10-diones (8a):

The reaction time was 7 days when formaldehyde was used and **8a** was obtained as red needles (210mg, 66%).m.p 188-190. IR (KBr): 3354(s), 1672(m),1618(s), 1504(s)cm^{-1}. ^{1}HNMR δ_H(acetone-d6): 4.62(s,2H), 4.90(s,2H), 7.30(br,NH),7.69(dt, J_1=7.5Hz,J_2=1.3Hz,1H), 7.78 (dt, , J_1=7.5Hz,J_2=1.3Hz,1H), 8.97(m,2H) . C-13 NMR δ: 63.01, 73.56, 112.54, 125.99, 126.06, 130.38, 132.18, 133.00, 134.61,142.61,179.93,180.07. m/z 215(M^+, 100%). Anal. Calcd. for $C_{12}H_9NO_3$: C,66.97;H,4.22; N,6.51. Found: C, 66.71; H, 4.12; N, 6.36.

1H-2,4-dihydro-2,4-dimethylnaphtho[2,3-d]1,3-oxazine-5,10-diones (8b) and (9b):

The reaction time was 2 days when acetaldehyde was used and **8b and 9b** were obtained as red crystals (237mg, 67%). m.p.213-215. IR(KBr): 3258(m), 1681(s), 1610(s), 1571(s), 1496(s), and 1382(m) cm^{-1}. ^{1}HNMR δ_H($CDCl_3$):1.51(m,6H), 5.03(dq,J_1=6Hz, J_2=1.7Hz, 1H), 5.10(q,J=7Hz,1H),5.88(br,NH), 7.59(m,1H), 7.69(m,1H), 7.99(m,1H), 8.05(1H) . Non-overlapping peaks for the minor isomer **9b** were present at 1.62(d, J=7Hz,3H), 4.77(dq,J_1=7Hz, J_2=1.7Hz, 1H), 4.93(q,J=7Hz,1H).). The ratio of the **8b** and **9b** isomers was determined to be 89.3: 10.7 respectively, by integration. C-13 NMR δ: 20.65,20.97,67.65, 72.60, 116.02, 125.82, 126.17, 130.34, 132.05, 133.27, 134.68, 141.81, 180.00, 180.39. m/z : 243(M^+, 61%). Anal. Calcd. for $C_{14}H_{13}NO_3$: C,69.13; H,5.39; N, 5.76. Found: C, 68.92; H, 5.30; N, 5.61.

1H-2,4-dihydro-2,4-diethylnaphtho[2,3-d]1,3-oxazine-5,10-diones (8c) and (9c):

The reaction time was 3 days when propanaldehyde was used and **8c and 9c** were obtained as red crystals (277mg, 70.4%). m.p.173-175. IR (KBr): 3270(m),1674(m),1608(s),1564(s),and 1498(s). ^{1}HNMR δ_H($CDCl_3$): 1.05(t,J=7.5Hz,3H), 1.08 (t, J=7.3 Hz),3H), 1.65 (m, 1H), 1.80(two quartets, J=7Hz, 2H),2.00(m,1H), 4.74(dt,J_1=6Hz ,J_2=1.5 Hz, 1H), 4.83(dd, J_1=11Hz, J_2=3Hz, 1H), 5.87(br,NH), 7.58(dt, J_1=7.5Hz,J_2=1.3Hz,1H), 7.68(dt,J_1=7.5Hz,J_2=1.3Hz,1H), 7.99(dd,J_1=7.5Hz,J_2=1.1Hz,1H), 8.05 (J_1=7.5Hz, J_2=1.1Hz, 1H). Non-overlapping peaks for the minor isomer **9c** were present at 0.95(t, J=7Hz,3H), 4.58(m, 1H), 4.93(q,J=7Hz,1H).). The ratio of the **8c** and **9c** isomers was determined to be 96: 4 respectively, by integration. m/z: 271(M^+,100 %). Anal. Calcd for $C_{16}H_{17}NO_3$: C,70.83; H,6.32; N,5.16. Found: C, 70.64; H, 6.12; N, 4.97.

1H-2,4-dihydro-2,4-dipropylnaphtho[2,3-d]1,3-oxazine-5,10-diones (8d) and (9d):

The reaction time was 5 days when propanaldehyde was used and **8d and 9d** were obtained as red crystals (275mg, 64%). m.p.142-143. IR (KBr): 3286(m),2956(m), 1674(m), 1606(s),1566(s), and 1492(s)cm^{-1}. ^{1}HNMR δ_H($CDCl_3$): 0.98(t,J=7.3Hz,3H), 0.99 (t, J=7.3 Hz),3H), 1.65 (m, 7H), 1.86(m, 1H),4.81(m,1H), 4.93(m , 1H), 5.85(br,NH), 5.87(br,NH), 7.57(dt, J_1=7.5Hz,J_2=1.3Hz,1H), 7.68(dt, , J_1=7.5 Hz, J_2=1.3Hz,1H), 7.98(dd, J_1=7.5Hz,J_2=1.1Hz, ,1H),8.04(J_1=7.5Hz,J_2=1.1Hz,1H). Non-overlapping peaks for the minor isomer **9d** were present at 0.91(t, J=7Hz,3H), 1.07(t, J=7Hz, 3H), 4.55(m, 1H), . The ratio of the **8d** and **9d** isomers

was determined to be 94: 6respectively, by integration. C-13 NMR δ:13.75,13.85,17.51,18.27,36.08,36.62, 71.11,75.62,115.54,125.87, 126.62,130.35,131.94,133.35,134.60,141.87,179.89,180.37. m/z: 299(M^+,100 %). Anal. Calcd for $C_{18}H_{21}NO_3$: C,72.22; H,7.07; N,4.68. Found: C, 72.35; H, 7.21; N, 4.53.

1H-2,4-dihydro-2,4-diisopropylnaphtho[2,3-d]1,3-oxazine-5,10-diones (8e) and (9e):

The reaction time was 5 days when isopropanaldehyde was used and **8d and 9d** were obtained as red crystals (230mg, 54%). The mixture was further chromatographed on silica gel using CH_2Cl_2as eluant to isolate the two isomers **8e** and **9e**. **8e**: Yield (170mg, 39%),m.p.117-119 IR (KBr): 3370(m),2960(m), 1674(m), 1606(s),1596(s),1564(s),1490(s), and 1364(m). ^{1}HNMR δ_H($CDCl_3$): 0.75(d,J=7Hz,3H), 1.06 (d , J=7Hz,3H), 1.07 (d, J=7Hz,3H),1.17(d,J=7Hz, 3H), 1.98(septet of doublet, J_1=7Hz, J_2=2.4 Hz,1H), 2.79 (septet of doublet, J_1=7Hz, J_2=2.4 Hz,1H), 4.39(dd,J_1=4.5Hz, J_2=1.7 Hz,1H), 4.78(d,J=2.4Hz, 1H), 5.85(br,NH), 7.59(m,1H), 7.70(m,1H), 8.00(m ,1H),8.06(m,1H). C-13 NMR δ:14.75,16.37,17.19,20.01,30.18,32.05,77.41, 84.39, 115.91,125.73, 126.23, 130.38,131.93,133.63, 134.59,145.27,180.16,180.27. Anal. Calcd for $C_{18}H_{21}NO_3$: C,72.22; H,7.07; N,4.68. Found: C, 72.12; H, 7.11; N, 4.54.

9e: Yield(60 mg, 14%).m.p. 126-128. IR (KBr): 3350(m), 1672(m), 1600(s),1570(s),1502(s), and 1372(m). ^{1}HNMR δ_H($CDCl_3$): 0.98(d,J=7Hz,3H), 1.05 (d , J=7Hz,6H), 1.08 (d, J=7Hz,3H), 1.97(septet of doublet, J_1=7Hz, J_2=1.8 Hz,1H), 2.07 (septet of doublet, J_1=7Hz, J_2=1.6 Hz,1H), 4.65(d,J=8.6Hz,1H), 4.71(dd,J_1=2.4Hz, J_2=1.2Hz,1H),6.02(br,NH),7.60(m,1H),7.71(m,1H),8.05(m,2H). C-13NMR δ: 16.32,17.30, 18.76,18.96,32.37 ,32.55,75.17,80.71,113.56,125.81,126.36,130.34,131.80,133.56,134.65,141.93,179.85,180.40. Anal. Calcd for $C_{18}H_{21}NO_3$: C,72.22; H,7.07; N,4.68. Found: C, 72.08; H, 7.02; N, 4.51.

1H-2,4-dihydro-2,4-dibutylnaphtho[2,3-d]1,3-oxazine-5,10-diones (8f) and (9f):

The reaction time was 3 days when pentaldehyde was used and **8f and 9f** were obtained as red crystals (270mg, 57%). m.p.133-134. IR (KBr): 3280(m),2932(m),1674(m),1608(s),1566(s), 1490(s),1378(s),and1330(m) cm^{-1}. ^{1}HNMR δ_H($CDCl_3$): 0.92(t,J=7.5Hz,3H), 0.94 (t, J=7.3 Hz),3H), 1.48 (m, 8H), 1.65(m, 1H),1.76(m,2H), 1.93(m,1H),4.80(m, 1H), 4.91(dd, J_1=11Hz, J_2=3Hz, 1H), 5.80(br,NH), 7.57(m,1H),7.67(m,1H), 8.02(m,1H). Non-overlapping peaks for the minor isomer **9f** were present at 0.87(t, J=7Hz,3H), 1.07(t,J=7Hz, 3H), 5.10(m,1H).). The ratio of the **8f** and **9f** isomers was determined to be 89: 11 respectively, by integration. C-13NMR δ: 13.88,22.29,26.19, 27.12, 33.58,34.25,71.25,75.72,115.55,125.84, 126.12,130.35,131.87,133.53,134.56,141.84,179.86,180.37. Anal. Calcd for $C_{20}H_{25}NO_3$: C,73.37; H,7.70; N,4.28. Found: C, 73.19; H, 7.62; N, 4.13.

2-Amino-3-(α-N-phenylmethyl-2`-amino-1`,4`-naphthoquinonyl)-1,4-naphthoquinone(11):

To a solution of 250mg (1.45 mmol) aminoquinone **1** and 1ml of bezalaldehyde (excess) in 50 ml of chloroform, triflouroacetic acid(3 drops) was added. The reaction mixture was stirred at 50˚ C for 3days. Then , the solvent was removed and the residue was recrystallized from CH_3OH to produce 150mg (24%) of **11**. m.p.238-239. IR (KBr): 3406(s), 1608(s), 1586(s),1494(m),1350(m), and 1298(m)cm^{-1}. ^{1}HNMR δ_H($CDCl_3$):

5.82(br,2H), 5.86(s,1H),6.15(d,J=6Hz,1H), 6.90(d,J=6Hz,1H),7.40(m,2H), 7.71(m,2H),8.01(m,3H), 8.12 (m,1H). C-13 NMRδ:52.78,102.93,112.78,126.03,126.20,126.40,126.76,128.11,129.17,130.11,130.53, 132.16, 132.48,132.87,133.41,134.72,134.96,138.04,145.68,147.49,181.27,181.73,182.04,183.40. m/z: 434(M^+, 100%). Anal. Calcd for $C_{27}H_{18}N_2O_4$: C,74.64; H,4.17; N,6.44. Found: C, 74.57; H, 4.12; N, 6.36.

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