The unusual transformation of 2-hydroxy-1-naphthaldehyde in reactions with morpholine

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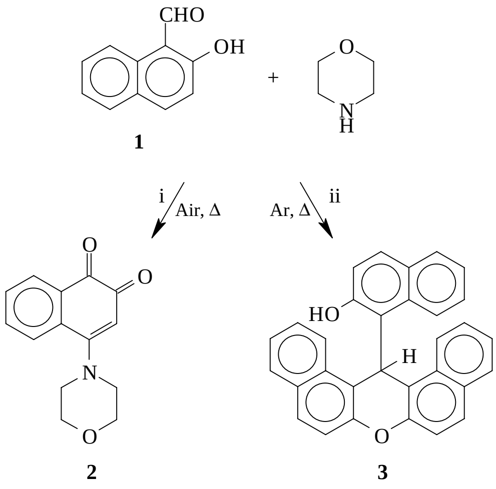
The reaction of 2-hydroxy-1-naphthaldehyde **1** with morpholine yields 4-*N*-morpholino-1,2-naphthoquinone **2** (in air) or 9*H*-dibenzo[*a*,*j*]-9-(2-hydroxynaphth-1-yl)xanthene **3** (in argon).

Aromatic aldehydes readily react with secondary amines to give aminals.[1] Salicylic aldehyde reacts with morpholine to give morpholinal with good yield.[2] Reactions of 2-hydroxy-1-naphthaldehyde **1** with morpholine may led to other results. It has been found that interaction of **1** with morpholine in air in the presence of water gives dark red crystals of 4-*N*-morpholino-1,2-naphthoquinone **2**. On the other hand, the reactions of **1** with morpholine under argon atmosphere yields the colorless crystalline 9*H*-dibenzo[*a*,*j*]-9-(2-hydroxynaphth-1-yl)xanthene **3** (Scheme 1).[†]

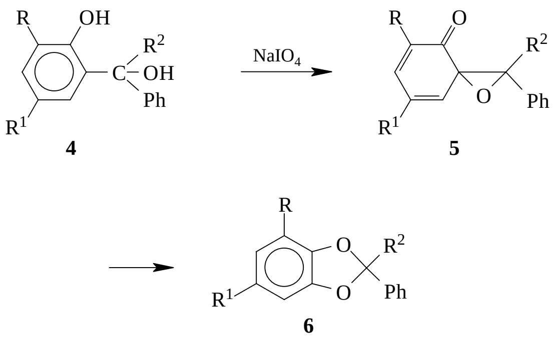
The structures of compounds **2** and **3** were confirmed by an X-ray structural study[‡] (Figure 1). Both reaction i and ii include decarbonylation of aldehyde **1**.

The oxidation of *o*-hydroxyalkylphenols **4** with $NaIO_4$ gives *exo*-epoxydienones **5** which undergo rearrangement into the cyclic acetals **6** (Scheme 2).[3]

Hemi-aminal **7** – an intermediate in interaction of **1** with morpholine[1] – and phenol **4** are structurally similar compounds.



Scheme 1



Scheme 2

We propose that **7** was oxidized by air oxygen to the aminoepoxydienone **8** (analogue of **5**) which further adds morpholine to the epoxy group. The interaction of intermediate **9** with morpholine and air oxygen and elimination of *tris*-morpholinemethane are final stages of reaction (Scheme 3).

Apparently, water is necessary for hydrolysis of morpholinal of aldehyde **1** to hemi-morpholinal **7**. The formation of compound **3** can be easily explained, if it will be supposed that morpholine in argon atmosphere reduces the hydroxyaldehyde **1** into β-naphthol (Scheme 4).

It is known,[4] that naphtholate anions are good C-nucleophiles and β-naphthol readily reacts with mild electrophiles. Recently[5] we reported on the interaction of **10** with 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde in morpholine media. These data allow us to suggest the reaction (Scheme 5).

[†] 4-*Morpholino*-1,2-*naphthoquinone* **2**. 1 g (0.0058 mol) of 2-hydroxy-1-naphthaldehyde, 2 ml (0.024 mol) of morpholine and 1 ml H_2O were put into a porcelain cup. The mixture was boiled for 1 min and kept during 12 h at room temperature. Deep-red product was twice recrystallised from Pr^iOH. Dark red crystals were obtained. Yield 0.5 g (35%), mp 201–203 °C (Lit. data:[6] mp 197 °C).

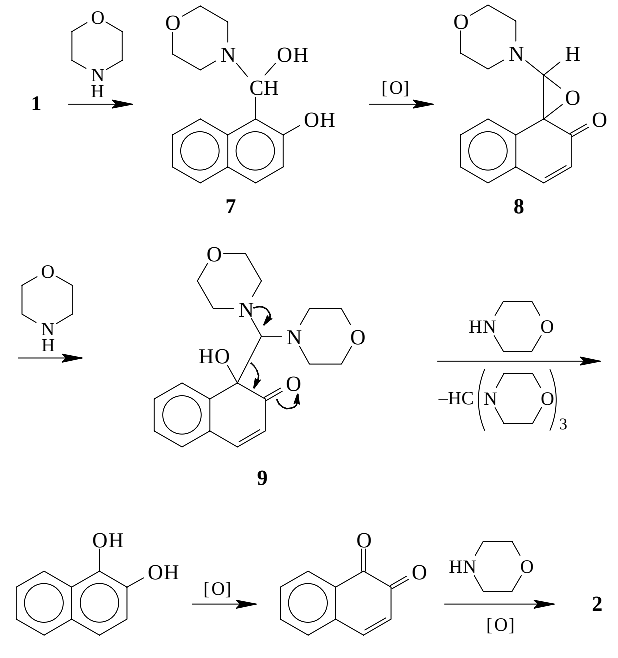
9*H-Dibenzo*[*a*,*j*]-9-(2-*hydroxynaphth*-1-*yl*)*xanthene* **3**. 2.58 g (0.015 mol) of 2-hydroxy-1-naphthaldehyde **1** was boiled for 1 h in morpholine (5 ml) under argon atmosphere and cooled. Pr^iOH (5 ml) and hexane (5 ml) were added to the reaction mixture. The precipitate was filtered off and recrystallized from acetonitrile to give a colorless adduct of compound **3** with acetonitrile (1:1) in 73% yield (1.7 g).

Compound **3** gave an adduct with Pr^iOH (1:1), but it crystallized from toluene without solvent; mp 273 °C (from toluene) (Lit. data:[7] mp 273 °C).

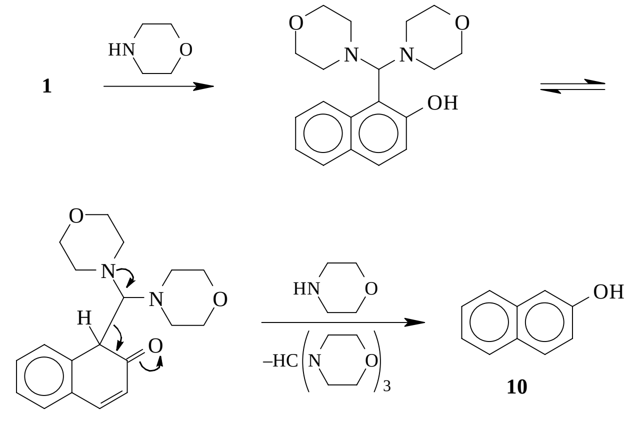
A satisfactory elemental analysis was obtained.

[‡] *Crystal data* for **2**: $C_{14}H_{13}NO_3$, monoclinic, space group $P2_1/c$, $a = 9.737(4)$, $b = 8.472(4)$, $c = 14.734(8)$ Å, $\beta = 108.80(5)°$, $V = 1150.6(6)$ Å^3, $F(000) = 512$, $D_c = 1.412$ g cm^{-3}, $Z = 4$. Data were measured using DAR-UM diffractometer ($T = 293$ K, graphite-monochromated CuKα radiation, $\lambda = 1.5405$ Å, $\theta/2\theta$ scan, $2\theta_{max} = 120°$). The structure was solved by direct method using RENTGEN-75 program. Anisotropic (isotropic for H-atoms) least-squares refinement against F converged at $R = 0.081$ for 1515 observed independent reflections with $I > 3\sigma(I)$.

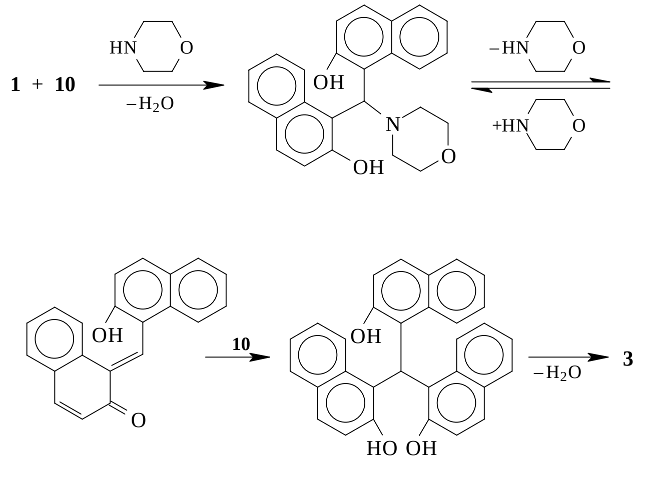
Crystal data for adduct **3** with Pr^iOH (i): $C_{31}H_{20}O_2{\cdot}C_3H_8O$, monoclinic, space group $P2_1/n$, $a = 7.959(3)$, $b = 17.481(6)$, $c = 18.731(6)$ Å, $\beta = 100.97(3)°$, $V = 2559(2)$ Å^3, $F(000) = 1024$, $D_c = 1.258$ g cm^{-3}, $Z = 4$. Data were measured using Siemens P3/PC diffractometer ($T = 293$ K, graphite-monochromated MoKα radiation, $\lambda = 0.71073$ Å, $\theta/2\theta$ scan, $2\theta_{max} = 50°$). The structure was solved by direct method using SHELXTL PLUS program package. Refinement against F^2 in anisotropic approximation (the hydrogen atoms isotropic in riding model) by full matrix least-squares method for 2565 reflections was carried out to $R1 = 0.086$ [for 1651 reflections with $F > 4\sigma(F)$, $wR2 = 0.283$, $S = 1.04$]. Atomic coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC), see Notice to Authors, *Mendeleev Commun.*, 1997, issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1135/21.



Scheme 3



Scheme 4



Scheme 5

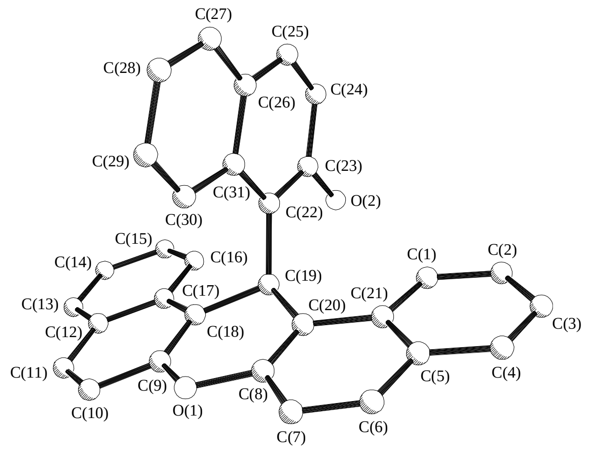


Figure 1 Molecular structure of **3** (hydrogen atoms are omitted for clarity). Selected bond lengths/Å: O(1)–C(8) 1.409(7), O(1)–C(9) 1.415(9), C(18)–C(19) 1.544(7), C(19)–C(20) 1.55(1), C(19)–C(22) 1.546(8), C(23)–O(2) 1.362(9).

In order to support the proposed mechanism, the synthesis of **3** according to this scheme was performed. It was found that heating compounds **1**,**10** and morpholine in molar ratio 1:2:3 under argon atmosphere at 140 °C during 15 min leads to compound **3** with 82% yield. In this case, compound **3** precipitated already after 5 min, but this compound precipitated only after 40 min in reaction 2 (without β-naphthol). These data are in agreement with the suggestion that hydroxyaldehyde **1** reduces into β-naphthol.

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