Unexpected transformation of 1,1′-methylenebis(2-naphthol) into 1,2,1′,2′-tetrahydrospiro(naphthalene-1,3′-naphtho[2,1-*b*]pyran)-2-one, a spirodimer of 1,2-naphthoquinone 1-methide, in the presence of boric acid and paraformaldehyde

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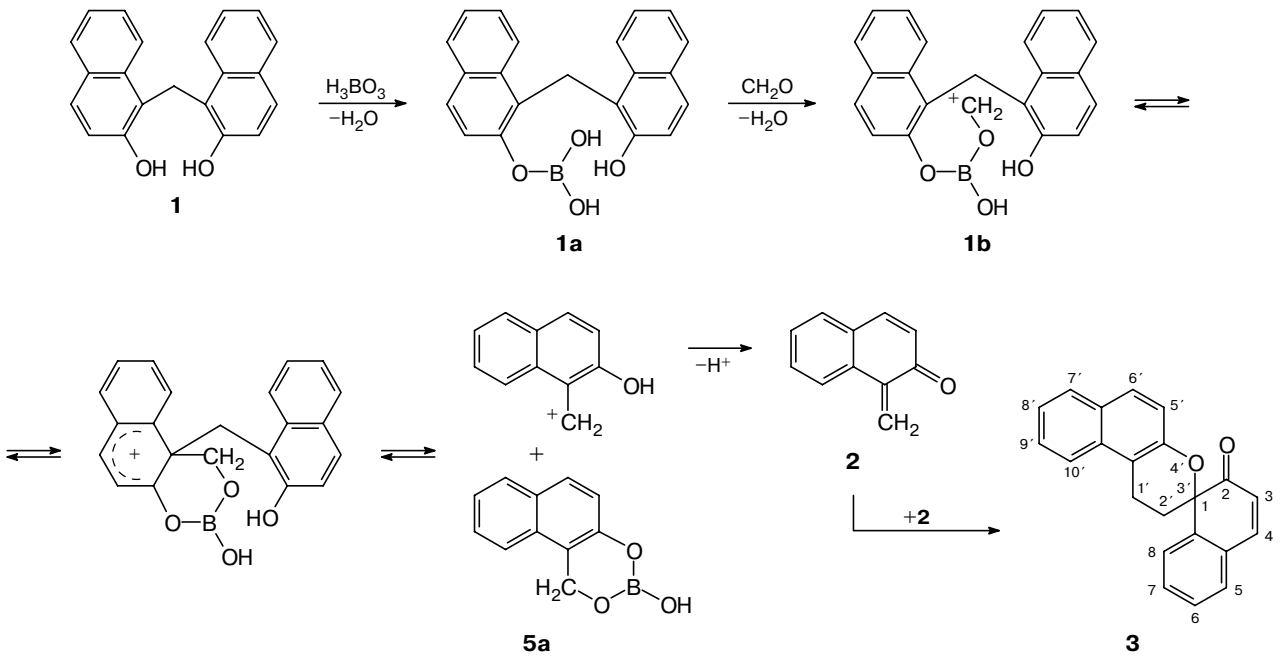
When heated in benzene with paraformaldehyde and boric acid, 1,1′-methylenebis(2-naphthol) easily decomposes to 1,2-naphthoquinone 1-methide, which dimerizes into a spirodimer. The by-product of the reaction is 14*H*-dibenzo[*a*,*j*]xanthene.

Key words: 1,1′-methylenebis(2-naphthol), paraformaldehyde, boric acid; 1,2-naphthoquinone 1-methide; 14*H*-dibenzo[*a*,*j*]xanthene.

We have recently[1] developed an efficient method for the synthesis of salicylic alcohols by *ortho*-hydroxymethylation of phenols with paraform in the presence of boric acid in boiling benzene with azeotropic removal of water. Under the same conditions, dinaphthylmethane **1** was found to be completely converted, like phenols, over 2.5 h (TLC) (Scheme 1). Unexpectedly, the reaction products were a spirodimer of 1,2-naphthoquinone

Scheme 1



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1-methide (**2**), namely, 1,2,1′,2′-tetrahydrospiro(naphthalene-1,3′-naphtho[2,1-*b*]pyran)-2-one (**3**) (41% yield), and 14*H*-dibenzo[*a*,*j*]xanthene (**4**) (5% yield).

Products **3** and **4** were isolated by alkaline treatment of the reaction mixture (see Experimental). It should be emphasized that substrate **1** (42% of the starting compound) reappeared during this procedure.

It is known that compound **3** is a dimer of unstable 1,2-naphthoquinone 1-methide (**2**), which is formed, *e.g.*, upon heating of 1-dialkylaminomethylene-[2–6] or 1-methoxymethylene-2-naphthols[7–9] above 180 °C in inert solvents. Thus, we revealed for the first time the possibility of generating quinone methide **2** from bisnaphthol **1** under mild conditions.

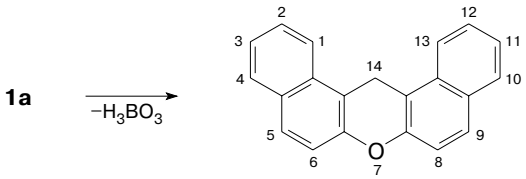
Boric acid and paraform are necessary because refluxing of bisnaphthol **1** in benzene in their absence or with boric acid alone does not yield compound **3**. When compound **1** is refluxed with paraform alone for 5.5 h, spirodimer **3** is formed in trace amounts, while xanthene (**4**) was not detected at all (TLC).

Before the final treatment, the reaction mixture contains another compound (R_f 0.40) different both from the starting bisnaphthol **1** (R_f 0.52) and from products **3** and **4**. All attempts to isolate this substance failed because it changed (completely or nearly so) to bisnaphthol **1**. In addition, when the chromatogram was treated with an aqueous solution of $FeCl_3$, a spot of this compound turned light blue, indicating the formation of chelates, which is a characteristic test for the hydroxymethyl group in *ortho*-position relative to the phenol hydroxy group. Based on these data, one can state that the compound under discussion is 1-hydroxymethyl-2-naphthol (**5**), which exists in the reaction mixture as a stable cyclic borate **5a**. It is known that alcohol **5** is quite labile, readily disproportionating to bisnaphthol **1** when heated above 185 °C [2] or 100 °C.[3] Because of such an easy conversion of **5** to bisnaphthol **1**, there are serious discrepancies between its melting points determined by different authors who attempted to obtain this compound from 2-naphthol and formaldehyde (188—200 °C)[2,10,11] or by reducing 2-hydroxy-1-naphthaldehyde (85.5 °C).[3]

All these data can be presented by a sequence of transformations in Scheme 1. The formation of borate **1a** and intermediate **1b** is similar to the known reactions of phenols and phenyl borates with formaldehyde.[12] The formation of quinone methide **2** and naphthyl borate **5a** is due to intramolecular electrophilic *ipso*-substitution in intermediate **1b**, as shown in Scheme 1.

The formation of xanthene **4** (see Scheme 2) is indirect evidence to the existence of intermediate naphthyl borate **1a**, since xanthene **4** is a product of intramolecular dehydration of the latter. To confirm this assumption, we obtained xanthene **4** by the reaction of bisnaphthol **1** with H_3BO_3 in boiling xylene without paraform in 6.6% yield, which is comparable with the yield according to Scheme 2 (5%). Therefore, paraform virtually does not affect the yield of product **4**, which is formed in parallel with the main process.

Scheme 2



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Thus, when heated with paraform and boric acid in benzene, 1,1′-methylenebis(2-naphthol) decomposes to 1,2-naphthoquinone 1-methide, whose dimerization gives 1,2,1′,2′-tetrahydrospiro(naphthalene-1,3′-naphtho[2,1-*b*]pyran)-2-one.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer (500.13 and 125.76 MHz, respectively) with $SiMe_4$ as the internal standard. Mass spectra were recorded on a Finnigan MAT 8200 instrument (EI, 70 eV, 280 °C). Melting points were determined on a Boetius instrument. The reaction mixtures were qualitatively analyzed by TLC in benzene—ethanol (9 : 1, by volume) using Silufol UV-254 plates. Spots were visualized in the UV light or by treating the plates with 5% $FeCl_3$ with subsequent heating. The starting compound **1** was prepared by condensation of paraformaldehyde with 2-naphthol.[11]

Reaction of 1,1′-methylenebis(2-naphthol) (1) with paraform and boric acid. A mixture of compound **1** (1.5 g, 5 mmol), H_3BO_3 (0.93 g, 15 mmol), and paraform (0.6 g, 20 mmol) in 70 mL of benzene was refluxed with removal of water for 1.5 h. Paraform (0.3 g, 10 mmol) was added, and the reaction mixture was heated for additional 1 h and then cooled. 1.6 *N* NaOH was added (50 mL), and the benzene layer was separated, washed with 1.6 *N* NaOH (10 mL) and water, and dried with Na_2SO_4. The solvent was removed at a reduced pressure, and the residue was chromatographed on silica gel in benzene to give a substance (0.1 g) with R_f 0.94. Its crystallization from EtOH gave xanthene **4** (0.07 g, 5%), m.p. 202 °C (Ref. 13: 203 °C).

^1H NMR (acetone-d_6), δ: 4.73 (s, 2 H, CH_2); 7.37 (d, 2 H, H(6), H(8), J = 8.8 Hz); 7.52 (td, 2 H, H(3), H(11), $J_1 = J_2$ = 8.0 Hz, J_3 = 1.5 Hz); 7.68 (td, 2 H, H(2), H(12), J_1 = 8.6 Hz, J_2 = 8.0 Hz, J_3 = 1.5 Hz); 7.90 (d, 2 H, H(5), H(9), J = 8.8 Hz); 7.95 (dd, 2 H, H(4), H(10), J_1 = 8.0 Hz, J_2 = 1.5 Hz); 8.27 (dd, 2 H, H(1), H(13), J_1 = 8.6 Hz, J_2 = 1.5 Hz). MS, *m*/*z*: 282 $[M]^+$; 281 [M − 1].

Further elution with benzene gave compound **3** (0.64 g, 41%) (R_f 0.81), m.p. 143 °C (EtOH) (Refs. 3, 6, and 9: 142—143 °C). ^1H NMR ($CDCl_3$), δ: 2.10—2.55 (m, 2 H, C(2′)H_2); 2.74—3.18 (m, 2 H, C(1′)H_2); 6.12 (d, 1 H, C(3)H, J = 10.0 Hz); 7.28—7.89 (m, 11 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 18.1 (C(1′)); 33.3 (C(2′)); 82.4 (C(3′)); 112.1 (C(10b′)); 116.4 (C(5′)); 129.3 (C(6a′)); 143.7 (C(4)); 143.8 (C(8a)); 152.4 (C(4a′)); 200.3 (C(2)); 121.7; 123.1, 123.4, 125.8, 126.1, 127.9, 128.2, 128.3, 128.9 (CH arom.); 129.3 (C arom.); 130.2 (CH arom.); 132.4 (C arom.).

The alkaline extract was acidified with conc. HCl to pH 4, and the product was extracted with ether. The extract was washed with water and dried with Na_2SO_4, and the solvent was

removed. The residue was recrystallized from xylene to give the starting compound **1** (0.63 g, 42%), m.p. 202 °C.

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