# A Simple Method of Generating Naphtho[1,2-*c*]furan and Naphtho[2,3-*c*]furan

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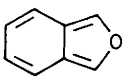
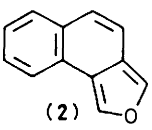
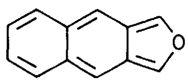
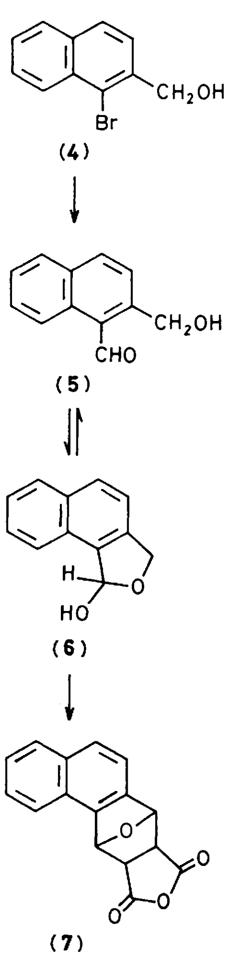
Naphtho[1,2-*c*]furan and the novel naphtho[2,3-*c*]furan have been generated from 2-(hydroxymethyl)-1-naphthaldehyde and 3-(hydroxymethyl)-2-naphthaldehyde, respectively, and trapped in Diels–Alder reactions with maleic anhydride.

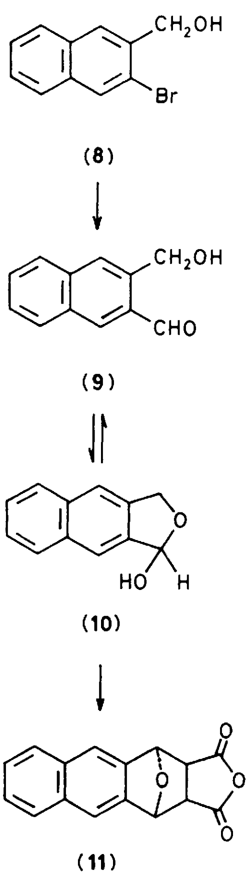
For some time we have been interested in the generation and synthetic utilization of isobenzofuran, (**1**), and its derivatives by the acid catalysed dehydration of 1-hydroxyphthalans.[1] As a consequence of this interest, it has been observed that there are significant structural effects on the equilibrium between the hydroxyphthalans (and their analogues) and the open chain tautomers. In order to extend both these studies, efforts have been made to prepare the benzo-analogues of isobenzofuran: naphtho[1,2-*c*]furan,[2] (**2**), and naphtho[2,3-*c*]furan, (**3**). In this communication, simple syntheses of 2-(hydroxymethyl)-1-naphthaldehyde, (**5**), and 3-(hydroxymethyl)-2-naphthaldehyde, (**9**), are described and evidence is presented that, as their cyclic tautomers, they can be dehydrated to generate the title compounds.


(1)


(2)


(3)





2-Methylnaphthalene was converted into 1-bromo-2-(bromomethyl)naphthalene by previously described literature procedures.[3,4] This benzylic halide was hydrolysed to 1-bromo-2-(hydroxymethyl)naphthalene, (**4**), (m.p. 101—102 °C, lit.[5] 103—104 °C), using KOH in 1 : 1 dioxane–water. Transmetallation of (**4**) using 3 equiv. of n-butyl-lithium in diethyl ether at − 78 °C and warming to 0 °C proceeded readily and the resulting aryl-lithium derivative was functionalized with *N*,*N*-dimethylformamide to produce 2-(hydroxymethyl)-1-naphthaldehyde, (**5**), in 27% overall yield. The 400 MHz $^1H$ n.m.r. spectrum of this compound in $CDCl_3$ [3.55 (br. s, 1H, exchanges with $D_2O$), 5.10 (d, *J* 13 Hz, 1H), 5.37 (dd, $J_1$ 13, $J_2$ 3 Hz, 1H), 6.89 (d, *J* 3 Hz, 1H), 7.2—8.0 (m, 6H)] shows only those signals due to the ring-closed tautomer, (**6**). The use of this compound to generate (**2**) was demonstrated by heating it in acetic acid at 100 °C in the presence of maleic anhydride. The *exo* Diels–Alder adduct, (**7**), was obtained in 70% yield.

2-Bromo-3-methylnaphthalene[6] was treated with 2 equiv. of *N*-bromosuccinimide in $CCl_4$ with a small amount of benzoyl peroxide to give 2-bromo-3-(dibromomethyl)naphthalene. This was hydrolysed using $CaCO_3$ in water[7] to give 3-bromo-2-naphthaldehyde, and then reduced with $NaBH_4$ to give 2-bromo-3-(hydroxymethyl)naphthalene, (**8**) (m.p. 113—115 °C, lit.[8] 95—100 °C). Conversion into 3-(hydroxymethyl)-2-naphthaldehyde, (**9**), was effected in a manner identical to the analogous reaction of (**4**). The 400 MHz $^1H$ n.m.r. spectrum of (**9**) in $CDCl_3$ showed it to be 80% ring-opened (**9**) and 20% ring-closed (**10**) [(**9**): 3.50 (br. s, 1H, exchanges with $D_2O$), 4.96 (s, 2H), 7.4—8.1 (m, 5H), 8.37 (s, 1H), 10.18 (s, 1H); (**10**): 5.18 (d, *J* 13 Hz, 1H), 5.40 (d, *J* 13 Hz, 1H), 6.62 (s, 1H), 7.4—8.1 (m, 6H)]. Treatment of this tautomeric mixture with maleic anhydride in acetic acid at 100 °C gave a 2 : 1 *endo–exo* mixture of Diels–Alder adduct (**11**) in 29% overall yield from 2-bromo-3-methylnaphthalene. To our knowledge, this represents the first demonstration of the existence of naphtho[2,3-*c*]furan.†

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† *Note added in proof.* Since submitting this manuscript, an alternative synthesis of (**3**) has appeared: B. Rickborn and B. Mir-Mohamed-Sadeghy, *J. Org. Chem.*, 1983, **48**, 2237.