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Electrophilic dimerization of naphthols in the presence of aluminum halides

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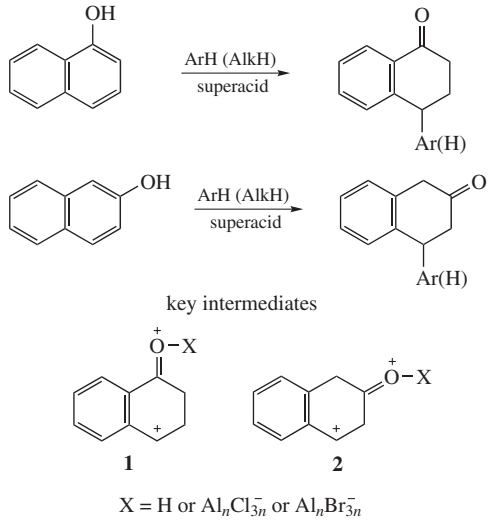
Naphthols undergo dimerization in the presence of an excess of aluminum halides to give mixtures of isomeric hydroxynaphthyltetralones.

Construction of binaphthyls is a challenging task in organic chemistry. Mostly they are accessed by oxidative coupling of naphthols and other electron-rich naphthalenes.[1] A notable example is the conversion of 2-naphthol into 1,1′-binaphthyl-2,2′-diol (BINOL), a valuable versatile chiral molecule having its (*R*)- and (*S*)-atropoisomers.[2] Another developed approach is based on organometallic chemistry, which offers various strategies for the synthesis of symmetrically and non-symmetrically substituted binaphthyl derivatives.[2(d),(e)]

In contrast, there are no reports in the literature on formation of binaphthyl framework *via* electrophilic aromatic substitution reactions. However, it is known that 1-naphthol reacts with some monoarenes under the influence of an excess of aluminum halides or in the HF–SbF_5 superacid medium to afford 4-aryl-1-tetralones (Scheme 1).[3] 2-Naphthol reacts analogously to give 4-aryl-2-tetralones (see Scheme 1).[4] Furthermore, selective ionic reduction of naphthols with alkanes leads to tetralones under similar reaction conditions.[5] The mechanism of these reactions was recognized to involve superelectrophilic[6] dications **1** and **2** as the key intermediates formed by C,C-diprotonation. A number of analogous dications have indeed been generated and detected as long-lived species by dissolving naphthols and/or their derivatives in liquid superacids.[7]

It seemed reasonable to employ this type of reactions for construction of binaphthyl skeleton. We anticipated that in the absence of nucleophiles such as arenes and alkanes, dications **1** and **2** could react with free naphthol existing in the reaction medium in low equilibrium concentrations. In this study, we disclose that 1- and 2-naphthols are indeed able to undergo dimerization under conditions of their dicationic activation.

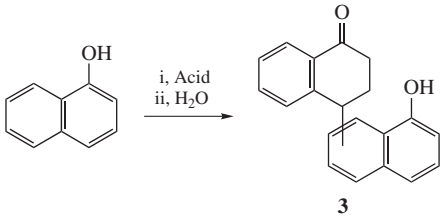


Scheme 1

Table 1 Electrophilic dimerization of 1-naphthol.

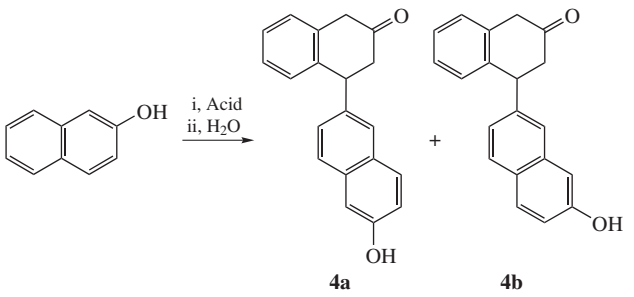
Entry	Acid (equiv.)	Time/h	Temperature/°C	Yield[a] (%)
1	$AlCl_3$ (1.0)–CH_2Cl_2	150	25	—[b]
2	$AlCl_3$ (3.5)–CH_2Cl_2	150	25	16[c]
3	$AlBr_3$ (3.5)–CH_2Br_2	24	25	35[c]
4	$AlBr_3$ (3.5)–CH_2Br_2	150	25	85[c]
5	$AlCl_3$ (3.0)	3	140[d]	11[e]
6	$AlCl_3$ (3.5)–$MeNO_2$	24	25	—[f]

[a] Overall yield of isomers **3** is given based on ^{1}H NMR spectroscopic data. [b] No reaction. [c] The balance is mainly unreacted 1-naphthol. [d] The melting conditions. [e] Complex mixture. [f] Oxidative oligomerization of 1-naphthol takes place.



Scheme 2

We first investigated the reactivity of 1-naphthol under various reaction conditions (Scheme 2, Table 1). In fact, 1-naphthol in the presence of an excess of aluminum halides formed mixtures of isomeric 4-(1-hydroxynaphthyl)-1-tetralones (general structure **3**). According to GC-MS data, the mixtures contain from 5 to 7 compounds with molecular ions of *m*/*z* 288 which corresponds to double weight relative to molecular weight of 1-naphthol (see Online Supplementary Materials). The IR spectra of the crude reaction mixtures show the intense bands at 1640–1690 cm^{-1} (C=O). NMR analysis of the reaction mixtures reveals the appearance of 4-aryl-1-tetralone moiety. Thus, the ^{1}H and ^{13}C NMR spectra (500 and 125 MHz, respectively) show the CH_2 and CHAr groups signals related to 1-tetralone fragments around δ_H 2.4, 2.7 and 4.2 ppm and δ_C 30, 35 and 45 ppm (see Online Supplementary Materials and *cf.* NMR spectra of 4-phenyltetralones[8]). In addition, ^{13}C NMR spectra exhibit 5–7 signals at δ 195–200 ppm, which belong to carbonyl groups of isomers **3**. However, none



Scheme 3

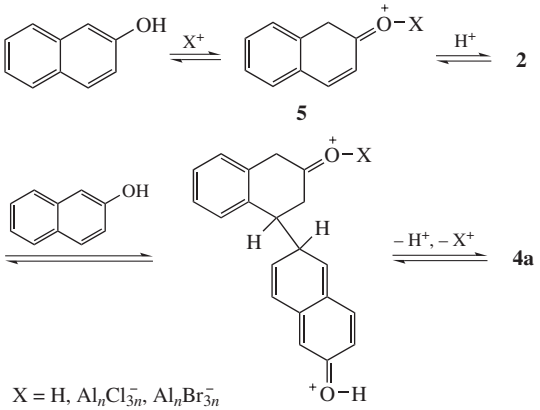
of the isomer is formed in predominance and it is difficult to separate the isomers. Obviously, this strongly limits the practical significance of the reaction.

2-Naphthol was observed to react more selectively giving isomeric 4-(2-hydroxynaphth-6-yl)-2-tetralone (**4a**) and 4-(2-hydroxynaphth-7-yl)-2-tetralone (**4b**) in ~3:1 ratio (Scheme 3, Table 2).† Notably, the reaction is highly selective under various reaction conditions, including melting of 2-naphthol/$AlCl_3$ mixtures at 140–170 °C (entries 1–9). The best results were achieved, however, when the reaction was mediated by *n*-butylpyridinium chloride/$AlCl_3$ ionic liquid[9] at room temperature (entries 10–12). The regioselectivity of the reaction is in accordance with known regioselectivity of the 2-naphthol electrophilic alkylation producing mainly 6-alkyl-2-naphthols.[10] The plausible mechanism of the reaction involves generation of dications **2** followed by their reaction with free form of 2-naphthol (Scheme 4). Dications **2** (X = H) have been previously detected by ^{1}H and ^{13}C NMR as long-lived species in HF–SbF_5–SO_2ClF superacid system at –40 °C.[7(b)] However, in the presence of aluminum halides, participation of dicationic species **2** (X = $Al_nHal_{3n}^-$, Hal = Cl, Br) seems more probable, as 2-naphthol is quantitatively converted into complexes **5** (X = $Al_nHal_{3n}^-$) upon action of $AlCl_3$ and $AlBr_3$.[11] The subsequent C-protonation of **5** results in formation of **2** in equilibrium with **5** and non-coordinated 2-naphthol. A catalytic amount of protic superacid (HHal–Al_nHal_{3n} or H_2O–Al_nHal_{3n}), which is required for C-protonation of intermediate species **5**, is normally present in such reaction media due to traces of water in the starting materials. So, additional saturation of the reaction mixture with gaseous HHal, which usually accelerates similar reactions,[12] is not generally needed. The acid strength of HHal–Al_nHal_{3n} (Hal = Br, Cl) is estimated to be –15 to –18 in *Ho* scale.[13]

Table 2 Electrophilic dimerization of 2-naphthol.

Entry	Acid (equiv.)	Time/h	Temperature/°C	Yield[a] (%)
1	$AlCl_3$ (1.0)	8	150[b]	—[c]
2	$AlCl_3$ (3.5)	2	150[b]	11[d]
3	$AlCl_3$ (3.5)	4	150[b]	18[d]
4	$AlCl_3$ (3.5)	8	150[b]	21[d]
5	$AlCl_3$ (5.0)	2	150[b]	15[d]
6	$AlCl_3$ (5.0)	5	150[b]	16[d]
7	$AlCl_3$ (5.0)	1	170[b]	5[d]
8	$AlCl_3$ (5.0)	4	170[b]	4[d]
9	$AlCl_3$ (5.0)–NaCl (1.5)	2	140[b]	20[d]
10	$AlCl_3$ (5.0)–BPC[e] (2.5)	4	25	8[d]
11	$AlCl_3$ (5.0)–BPC[e] (2.5)	30	25	25[d]
12	$AlCl_3$ (5.0)–BPC[e] (2.5)	72	25	14[f]
13	$AlBr_3$ (3.5)–CH_2Br_2	170	25	10[f]
14	$AlCl_3$ (3.5)–$MeNO_2$	100	25	—[g]
15	$AlCl_3$ (3.5)–$MeNO_2$	480	25	—[h]

[a] Overall yield of isomers **4** is given based on ^{1}H NMR spectroscopic data. The ratio of **4a** : **4b** is about 3:1 in each case. [b] The melting conditions. [c] No reaction. [d] The balance is unreacted 2-naphthol. [e] *n*-Butylpyridinium chloride. [f] Complex mixture. [g] Mixture of BINOL and **6** in ~2:1 molar ratio is obtained. [h] Mixture of BINOL and **6** in ~1:1 molar ratio is obtained.



Scheme 4

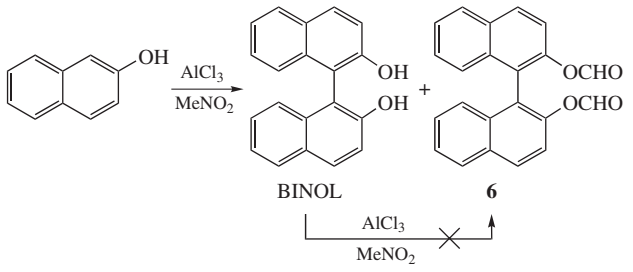
Taking into account a quantitative recovery of unreacted 2-naphthol and weak influence of the reaction time on the result of reaction, it seems very likely that the moderate yield of dimers **4** (no more than 25%, see Table 2) is close to the equilibrium concentration of the product. In agreement with this assumption, reaction of **4** with *n*-butylpyridinium chloride/$AlCl_3$ ionic liquid (the molar ratio 1:2.5:5, respectively) gave a mixture of **4** and 2-naphthol (~1:5) over a 24 h period at 25 °C. The sensitivity of the reaction to the reverse process is in agreement with the known reactivity of 2-naphthol towards benzene and *o*-dichlorobenzene.[4] According to theoretical (DFT) calculations, dication **2** (X = H) is less electrophilic compared to diprotonated form of 1-naphthol (structure **1**, X = H).[14] This explains the increased conversion of 1-naphthol relative to that of 2-naphthol under comparable reaction conditions (Tables 1 and 2). On the other hand, the substantial reactivity of dications **1** resulted in poor regioselectivity in the dimerization of 1-naphthol.

It should be noted that a 3–5-fold molar excess of aluminum halides is not essential and a decrease in the loading is possible. This, however, slows down the reaction. Moreover, the use of less than a ~2-fold molar excess of $AlCl_3$ or $AlBr_3$ can totally suppress the reaction (Tables 1 and 2). Obviously, the excess of aluminum halides is necessary to form dications **1** and **2**,[3,4] whereas generation of monocationic species, such as **5** does not require excess

† *4-(2-Hydroxynaphth-6-yl)-2-tetralone* **4a** *and 4-(2-hydroxynaphth-7-yl)-2-tetralone* **4b** *(typical procedure)*. A mixture of powdered $AlCl_3$ (freshly sublimed, 6 g, 22.5 mmol) and 2-naphthol (1 g, 6.25 mmol) was stirred and heated at 150 °C for 8 h. The dark-green melt was cooled and carefully treated with ice and dilute HCl. The resulting mixture was extracted with diethyl ether. The organic phase was washed several times with water, then dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to obtain the crude product consisting of a mixture of 2-naphthol, isomers **4a** and **4b** in 88:9:3 molar ratio (^{1}H NMR data). 2-Naphthol was removed by silica gel chromatography (benzene–acetone, 5:1) to give mixture of **4a** and **4b** (viscous solid, 0.14 g, 14%). HRMS, *m/z*: 288.1146 (calc. for $C_{20}H_{16}O_2$, *m/z*: 288.1150).

For **4a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.97 (dd, 1H, *J* 16.7 and 5.3 Hz), 3.07 (dd, 1H, *J* 16.7 and 7.5 Hz), 3.67 (d, 1H, *J* 20.3 Hz), 3.73 (d, 1H, *J* 20.3 Hz), 4.58 (t, 1H, *J* 6.8 Hz), 7.05–7.13 (m, 3H), 7.20–7.30 (m, 4H), 7.44 (s, 1H), 7.63 (d, 1H, *J* 8.5 Hz), 7.64 (d, 1H, *J* 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 44.7, 45.0, 45.9, 109.5, 118.3, 126.5, 126.8, 127.2, 127.3, 127.5, 128.4, 128.7, 129.0, 129.8, 133.4, 133.7, 136.5, 139.4, 153.7, 211.1.

For **4b** (fragmentary data were taken from the spectra of the mixture of products **4a** and **4b**): ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.96 (dd, 1H, *J* 16.7 and 5.3 Hz), 3.06 (dd, 1H, *J* 16.7 and 7.5 Hz), 3.66 (d, 1H, *J* 20.3 Hz), 3.73 (d, 1H, *J* 20.3 Hz), 4.58 (t, 1H, *J* 6.8 Hz), 7.05–7.30 (m, 7H), 7.37 (s, 1H), 7.72 (d, 1H, *J* = 8.5 Hz), 7.75 (d, 1H, *J* 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 44.9, 45.01, 45.8, 109.6, 117.9.



Scheme 5

of aluminum halides.[11] Therefore, participation of the latter as possible alternative key intermediate is unfeasible.

Note also that instead of electrophilic reactions, the use of $AlCl_3$/nitromethane medium leads to oxidative coupling of naphthols as a result of Scholl-type[1(*b*),15] reactions (Table 1, entry 6; Table 2, entries 14, 15). Remarkably, 2-naphthol gives BINOL and its diformate **6** (Scheme 5).‡ The latter is likely produced through formylation of BINOL with an *in situ* formed formic acid derivative, generated from nitromethane in the course of the coupling reaction. Indeed, our attempts to directly formylate BINOL with $AlCl_3$/nitromethane were unsuccessful. Close literature precedent exists for formylation of BINOL with such formic acid derivative as *N*,*N*-diformylacetamide.[16] Nevertheless, the mechanism of the formation of **6**, as well as synthetic significance of this reaction is presently unclear and special investigation for these matters is required.

In conclusion, 1- and 2-naphthols undergo dimerization under conditions that ensure their dicationic activation, in the presence of an excess of aluminum halides. Dimerization of 1-naphthol is not regioselective and gives complex mixture of isomers **3**. In contrast, 2-naphthol affords mainly dimer **4a**, although the yield is moderate because of the reaction reversibility. Despite the modest initial results, both reactions exemplify a new approach which can be of interest for the synthesis of non-symmetrically functionalized binaphthyls. Evidently, in addition to the parent naphthols, their derivatives may also exhibit analogous behavior. The extension of this synthetic concept is now under way and will be reported in due course.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2014.02.020.

‡ The diester **6** is a known compound;[16(*a*)] spectroscopic data are listed here as an update. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.22 (d, 1H, *J* 8.5 Hz), 7.38 (t, 1H, *J* 8.5 Hz), 7.54 (t, 1H, *J* 8.2 Hz), 7.80 (d, 1H, *J* 8.2 Hz), 7.81 (d, 1H, *J* 8.9 Hz), 7.97 (d, 1H, *J* 8.9 Hz), 9.18 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 117.7, 119.1, 120.3, 123.8, 127.7, 129.3, 132.1, 132.8, 150.1, 157.9. GC-MS, *m*/*z*: 342 $[M]^+$.

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