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Oxidative coupling of 2-substituted 1,2-dihydro-1-naphthols using Jones reagent: a simple entry into 3,3′-disubstituted 1,1′-binaphthyl-4,4′-diols

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Abstract—2-Substituted 1,2-dihydro-1-naphthols underwent regioselective oxidative dimerization, when treated with Jones reagent, to furnish 3,3′-disubstituted 1,1′-binaphthyl-4,4′-diols. A series of symmetrical binaphthols were prepared and it was shown that the coupling reaction proceeds via the sequential oxidation of 2-substituted 1,2-dihydro-1-naphthols to 2-substituted 1-naphthols, which oxidatively dehydrodimerized.

Binaphthyls are found in bioactive natural products[1] and play a significant role in asymmetric synthesis, acting as chiral ligands in a wide array of metal-mediated transformations. The importance of that structural motif has led to the development of numerous aryl–aryl coupling methodologies.[2] Most of the interest and efforts have been directed toward the preparation of 1,1′-binaphthyl-2,2′-diols, privileged ligands in asymmetric catalysis.[3] One of the most attractive and expedient approaches for binaphthol synthesis is the oxidative coupling of naphthols. Dehydrodimerization methods are preferable since no additional steps are required for the regioselective introduction of halides or pseudohalides.[4] A number of highly regio and enantioselective protocols to prepare 1,1′-binaphthyl-2,2′-diols from 2-naphthols using various promoters have been reported.[3] 1,1′-Binaphthyl-4,4′-diol synthesis by oxidative coupling of 1-naphthols has been scarcely investigated and mixtures of regioisomers are generally obtained.[5] These highly colorful compounds have been found to be useful as dyes and as key components in the synthesis of thermotropic liquid crystalline polyesters.[6] This communication outlines our results on the regioselective oxidative dehydrodimerization of 2-substituted 1,2-dihydro-1-naphthols using Jones reagent under mild conditions. Chen and Martin recently described the synthesis of 2-substituted 1-naphthols by oxidation of 2-substituted 1,2-dihydro-1-naphthols with IBX.[7] This work has prompted us to report our results concerning the dimerization of 2-substituted 1,2-dihydro-1-naphthols to 3,3′-disubstituted-1,1′-binaphthyl-4,4′-diols using Jones reagent.

During our studies on the preparation and reactivity of organodimetallic compounds, a convenient protocol to synthesize 2-alkynyl-1-naphthyl trifluoromethanesulfonate was required.[8] It was envisaged that these compounds could be readily accessed on gram-scale by oxidation of 2-substituted 1,2-dihydro-1-naphthols to the corresponding 1-naphthols, followed by triflation. Two examples of oxidation of 1,2-dihydro-1-naphthol derivatives using freshly recrystallized DDQ were previously reported by Martin and coworkers in their work on the synthesis of C-aryl glycoside antibiotics.[9] Moreover, 2-substituted 1,2-dihydro-1-naphthols are readily available by ring-opening of oxabenzonorbornadiene derivatives with organolithium and Grignard reagents.[10]

1,2-Dihydronaphthol **1a** was prepared by the addition of (5-lithio-1-pentynyl)trimethylsilane (prepared from (5-iodo-1-pentynyl)trimethylsilane and *t*-BuLi) to 1,4-dihydronaphthalene 1,4-oxide in 64% yield, followed by terminal alkyne deprotection with TBAF (98% yield). Initial attempts at oxidizing **1a** with the Swern protocol

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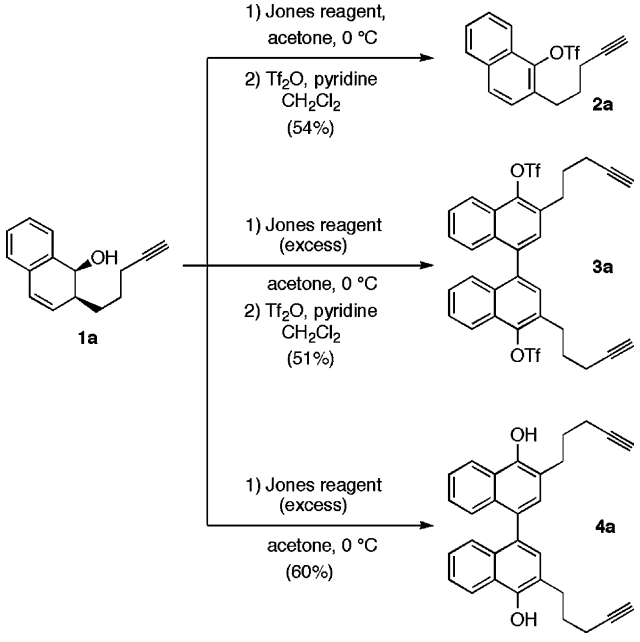
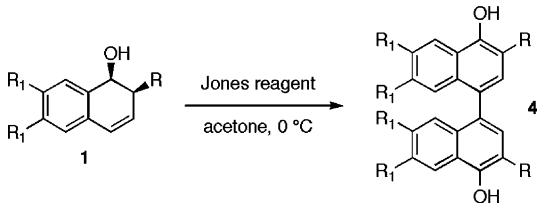
or TPAP/NMO failed to provide 2-(4-pentynyl)-1-naphthol, leading to the formation of 2-(4-pentynyl)naphthalene via elimination of the labile secondary benzylic alcohol, or to decomposition, respectively. Oxidation of **1a** with MnO_2 or PCC gave 2-(4-pentynyl)-1,4-dihydro-1,4-naphthalenedione. Unexpectedly, the highly acidic Jones reagent in acetone cleanly oxidized dihydronaphthol **1a** to the corresponding 1-naphthol, which was subsequently triflated to furnish 1-naphthyl triflate **2a** in 54% yield for the two-step sequence (Scheme 1).

The synthesis of naphthyl triflate **2a** was difficult to reproduce on gram-scale and generally provided exclusively symmetrical dimeric triflate **3a**. It was determined that the dimerization occurred during the oxidation step with Jones reagent by isolating 3,3′-bis(1-pentyn-5-yl)-1,1′-binaphthyl-4,4′diol **4a** in 60% yield (Scheme 1). Excess Jones reagent was thus suspected to promote dimerization of the resulting 1-naphthols. The quantity of Jones reagent required to carry out the oxidation was determined by monitoring both the changes in the reaction mixture color form orange to green and back to orange and the starting material consumption by TLC. Product **2a** was obtained when the oxidation was performed on small scale (100 mg) and Jones reagent was added dropwise until complete consumption of the starting material. Note that the color of the final solution was green. On larger scale, however, due to the reaction mixture opacity, the end point was difficult to determine which resulted in the addition of excess Jones reagent and dimer formation. The dimers had, in all cases, the same polarity as the 1-naphthols, and their formation could not be monitored by TLC. Thus, adding Jones reagent to 2-substituted 1,2-dihydro-1-naphthols in acetone until the orange color persisted, smoothly furnished the oxidative coupling products.



Scheme 1.

Table 1. Oxidative dehydrodimerization of 2-substituted 1,2-dihydro-1-naphthols

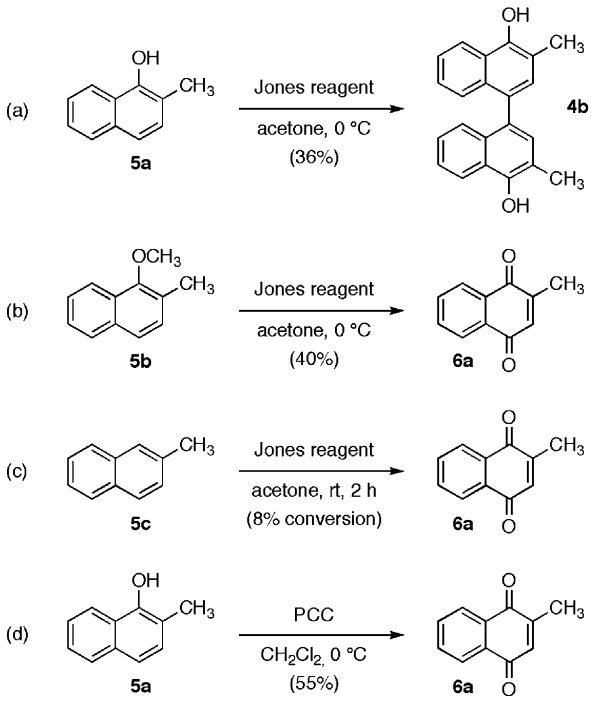


Entry	Substrate	R	R_1	Product	Yield[a] (%)
1	**1b**	Me	H	**4b**	68
2	**1c**	*n*-Bu	H	**4c**	54
3	**1d**	*t*-Bu	H	**4d**	61[b]
4	**1e**	Ph	H	**4e**	81
5	**1f**	$(CH_2)_2CCH$	H	**4f**	52
6	**1g**	Bu	Me	**4g**	28 (42)[c]

[a] Isolated yield.
[b] Isolated as an inseparable mixture of binaphthol:naphthalenedione (1:1).
[c] Isolated as the dimethoxy derivative following methylation of the crude binaphthol **4g** with MeI and K_2CO_3.

The operational simplicity and mildness of this dehydrodimerization reactions were incitements to investigate the scope of the process. As depicted in Table 1, the dimerization procedure was applied to a variety of 2-substituted 1,2-dihydro-1-naphthols.[11] Yields varied from 28% to 81% depending on the steric hindrance and the electronic nature of the substituent at the 2-position of the dihydronaphthol. In all cases, the main byproduct was the corresponding 2-substituted 1,4-dihydro-1,4-naphthalenedione.[12] The lower yield for the preparation of dimer **4d** and its unsuccessful purification may be attributed to its instability and rapid conversion on silica gel, in the presence of oxygen and light, to 2-*tert*-butyl-1,4-naphthoquinone (Table 1, entry 3). In general, 3,3′-disubstituted-1,1′-binaphthyl-4,4′-diols slowly converted to the corresponding naphthoquinones over time, and necessitated appropriate storage in the cold, in an amber flask, under an inert atmosphere of nitrogen or argon. Flash chromatography purification of dimer **4g** was tedious, but treatment of the crude reaction mixture with excess methyl iodide facilitated the isolation of the dimer as its dimethoxy analog in 42% yield (Table 1, entry 6).

As mentioned above, the oxidative dehydrodimerization of 1,2-dihydro-1-naphthols was postulated to proceed via two consecutive oxidation reactions promoted by Jones reagent; oxidation of the dihydronaphthols to the corresponding 1-naphthols followed by oxidative dimerization. In support of this hypothesis, the dimerization of 2-methyl-1-naphthol (**5a**) with Jones reagent was shown to provide dimer **4b** (Scheme 2). Mechanistic insights were further obtained from the failed attempt to dimerize 1-methoxy-2-methylnaphthalene (**5b**), which led to 2-methyl-1,4-naphthoquinone (**6a**). This result may suggest that the dimerization process involves chromate ester intermediates, generated in the strongly acidic medium by the attack of 1-naphthol on chromic



Scheme 2.

acid. The importance of the naphtholic group in the dimerization process was further established by reacting 2-methylnaphthalene (**5c**) with Jones reagent. After 2 h at room temperature, a clean but low 8% conversion to 2-methyl-1,4-naphthoquinone (**6a**) was determined by analysis of the crude ^{1}H NMR and GC-MS. The requirement for strong acidic conditions was demonstrated by the incapacity of PCC in dichloromethane to promote dimerization (Scheme 2).

In summary, a mild and operationally simple protocol to prepare 3,3′-disubstituted 1,1′-binaphthyl-4,4′-diols from 2-substituted 1,2-dihydro-1-naphthols was described.

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11. *Jones reagent preparation*: CrO_3 (13.66 g) in H_2O (20 mL) was placed in a 50 mL volumetric flask. H_2SO_4 95–98% (11.5 mL) was added with cooling. The mixture was then diluted to a total volume of 50 mL with water. *2-(5-Pentynyl)-1-naphthyl trifluoromethanesulfonate* (**2a**). To a solution of dihydronaphthol **1a** (100 mg, 0.471 mmol) in acetone (3 mL) cooled to 0 °C was added Jones reagent in a dropwise manner until disappearance of the starting material, as monitored by TLC. The reaction was quenched by the addition of isopropanol, followed by saturated $NaHCO_3$. The solution was extracted three times with Et_2O and the combined organics were washed with water, brine, dried over $MgSO_4$, and filtered. The solvent was removed in vacuo and the residue was azeotropically dried over benzene and taken directly to the next step without further purification. Triflation was carried out using pyridine (225 μL, 2.78 mmol) and triflic anhydride (141 μL, 0.838 mmol) in CH_2Cl_2 (2 mL). Purification by flash chromatography using hexanes–Et_2O (95:5) gave rise to an overall yield of 54% of **2a** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (1H, d, J = 8.5 Hz), 7.85 (1H, d, J = 8.2 Hz), 7.81 (1H, d, J = 8.5 Hz), 7.59 (1H, dt, J = 7.7, 0.9 Hz), 7.53 (1H, t, J = 7.5 Hz), 7.41 (1H, d, J = 8.5 Hz), 3.02 (2H, t, J = 7.8 Hz), 2.25 (2H, dt, J = 7.0, 2.6 Hz), 2.00 (1H, t, J = 2.6 Hz), 1.93 (2H, tt, J = 7.4, 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 133.7, 132.0, 128.6, 127.9, 127.7, 127.7, 126.6, 121.2, 118.8 (CF_3, q, J = 318 Hz), 83.4, 69.1, 29.4, 28.7, 18.1. Anal. Calcd for $C_{16}H_{13}F_3O_3S$: C, 56.14; H, 3.83. Found: C, 56.21; H, 3.88. *General procedure for the oxidative coupling of 2-substituted 1,2-dihydro-1-naphthols.* Jones reagent was added dropwise to a solution of 2-substituted 1,2-dihydro-1-naphthol in acetone cooled at 0 °C, until an orange color persisted. Two to three additional drops were added to the resulting mixture. Two work-up procedures were used.

The reaction was quenched with solid $NaHCO_3$, dried over $MgSO_4$, and then filtered over a pad of silica gel. Alternatively, the reaction was quenched with isopropanol, and the volatiles evaporated. The residue was suspended in Et_2O or EtOAc and filtered over silica, eluting until the filtrate came out colorless. The resulting solution was then washed with saturated $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography on silica gel. *3,3′-Bis(4-pentynyl)-1,1′-binaphthyl 4,4′-ditrifluoromethanesulfonate* (**3a**). Obtained as an off white solid, mp 107.0–108.5 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ 8.19 (1H, d, J = 8.6 Hz), 7.77 (1H, dt, J = 6.9, 1.4 Hz), 7.69 (1H, s), 7.48 (1H, dt, J = 6.9, 1.3 Hz), 7.34 (1H, d, J = 8.5 Hz), 3.19–3.16 (2H, m), 2.36 (1H, t, J = 2.7 Hz), 2.30 (2H, dt, J = 7.0, 2.6 Hz), 2.07–2.02 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3, 137.8, 132.8, 131.6, 129.7, 127.9, 127.3, 127.1, 126.4, 121.6, 120.9, 116.6 (CF_3, q, J = 320 Hz), 83.2, 69.3, 29.5, 28.7, 18.2; HRMS calcd for $C_{32}H_{24}O_6S_2F_6$: 682.0918. Found: 682.0904. *3,3′-Bis(4-pentynyl)-1,1′-binaphthyl-4,4′-diol* (**4a**). The crude ^{1}H NMR showed a 92:8 dimer to quinone ratio. Obtained as a red gum; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (1H, d, J = 8.4 Hz), 7.52–7.46 (1H, m), 7.39–7.36 (1H, m), 7.29 (1H, dd, J = 7.0, 1.1 Hz), 7.26 (1H, s), 5.67 (1H, br s), 3.00 (2H, t, J = 7.2 Hz), 2.32 (2H, dt, J = 6.7, 2.6 Hz), 2.16 (1H, t, J = 2.6 Hz), 1.98 (2H, quint, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4, 132.9, 131.0, 130.2, 126.5, 125.7, 125.2, 124.6, 121.4, 119.4, 84.4, 69.8, 28.6, 28.0, 17.6; HRMS calcd for $C_{30}H_{26}O_2$: 418.1933. Found: 418.1929. *3,3′-Bis(3-butynyl)-1,1′-binaphthyl-4,4′-diol* (**4f**). The crude ^{1}H NMR showed a 91:9 dimer to quinone ratio. Obtained as a dark red solid, mp 73.5–74 °C (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (1H, d, J = 8.4 Hz), 7.48 (1H, app. t), 7.39 (1H, d, J = 8.2 Hz), 7.28 (2H, m), 5.96 (1H, s), 3.09 (2H, d, J = 6.9 Hz), 2.63 (2H, dt, J = 6.9, 2.5 Hz), 2.11 (1H, t, J = 2.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6, 133.1, 131.1, 130.4, 126.6, 125.7, 125.3, 125.0, 121.3, 119.9, 84.6, 66.4, 29.8, 13.7; HRMS calcd for $C_{28}H_{22}O_2$: 390.1620. Found: 390.1626.

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