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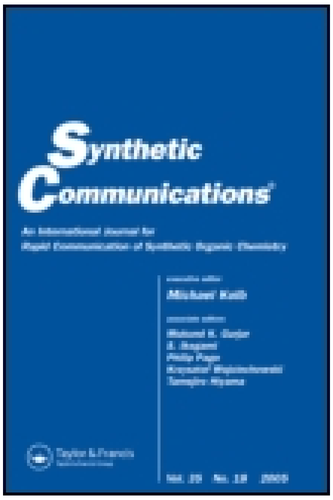

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SYNTHESIS OF (±) BINAPHTHOLS VIA OXIDATIVE COUPLING OF NAPHTHOLS BY CERIUM AMMONIUM NITRATE (CAN)

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SYNTHESIS OF (±) BINAPHTHOLS VIA OXIDATIVE COUPLING OF NAPHTHOLS BY CERIUM AMMONIUM NITRATE (CAN)

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ABSTRACT

2-Naphthol and methyl 3-hydroxy-2-naphthoate were oxidized to give the corresponding (±) binaphthols by cerium ammonium nitrate (CAN) in good yields.

Chiral binaphthol derivatives have been extensively used in stereoselective synthesis (1). Resolution of (±) binaphthols is a common method for obtaining this chiral reagent (2). (±) Binaphthols have been synthsized by direct oxidative coupling of 2-naphthols using Fe (III) (3), Mn (III) (4–6), and Cu (II) (7) salts. We report herein that cerium ammonium nitrate (CAN) is also an effective oxidative coupling reagent for 2-naphthols (Scheme 1).

It was found that CAN can oxidize 2-naphthols (1a, 2a) to give (±) binaphthols (1b, 2b) in high yield (∼90%) quickly at room temperature in either MeOH or acetonitrile (Table 1).

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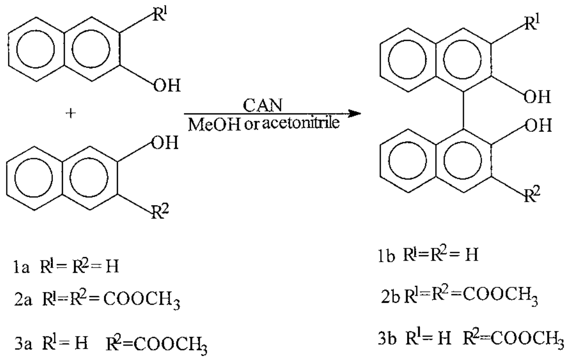


Scheme 1.

It should be pointed out that CAN is a less suitable oxidation reagent for the cross-coupling reaction of 2-naphthol with methyl 3-hydroxy-2-naphthoate. A 1:1 mixture (3a) gave only 47% of the cross-coupling oxidative product 3b, together with the coupling products 1b (22%) and 2b (25%). The statistical distribution of the products in the reaction of 2-naphthol with methyl 3-hydroxy-2-naphthoate (the approximate molar ratio of 1b:2b:3b is 1:1:2) suggests that the oxidative coupling reaction of 2-naphthols by CAN may proceed via a free-radical mechanism as shown in Scheme 2.

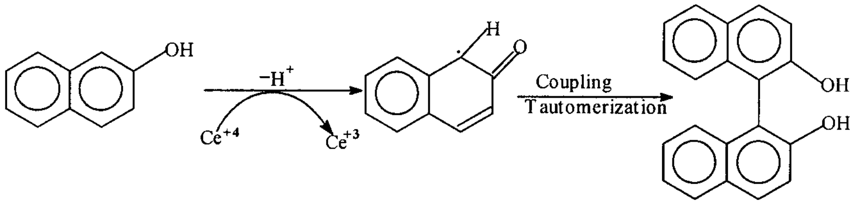
EXPERIMENTAL

Melting points were uncorrected. ^{1}HNMR spectra were recorded at a Bruker AM 400 spectrometer in $CDCl_3$ using TMS as internal standard. IR spectra were obtained using KBr pellets on a Nicolet 10DX FT-IR spectrophotometer. Analytical

Table 1. Yield of Coupling Products of 2-Naphthols

Substrate	Solvent	Product	Yield[a] (%)	M.P (°C)	Temp (°C)	Time (min)
1a	MeOH	1b	92	215	r. t	10
1a	Acetonitrile	1b	89	216	r. t	10
2a	MeOH	2b	94	234	r. t	15
2a	Acetonitrile	2b	90	234	r. t	15
3a	MeOH	3b	47	182	r. t	10

[a] Isolated yield.



Scheme 2.

thin layer chromatography (TLC) was performed on silica gel (precoated silica gel plate F_{254}, Merck) and visualized with a UV lamp.

General Procedure

2-Naphthol (1a, 0.38 g, 2.5 mmol) was dissolved in 20 mL of MeOH at room temperature. Nitrogen was bubbled through the solution, into which CAN (1.39 g, 2.53 mmol) in 15 mL of MeOH was added with stirring until the mixture turned reddish. The mixture was evaporated in vacuo and the residue was poured into 100 mL of H_2O at 0°C and filtered. The crude product was purified by silica gel chromatography using a petroleum ether-diethyl ether (3:1, v:v) as eluant.

Analytical Data for the Products

1b: white crystalline solid. M.p: 215°C (lit. (9): 214–217°C). IR (KBr, cm^{-1}): $\nu = 3404, 3485$. ^{1}HNMR ($CDCl_3$, ppm): $\delta = 7.25$ (m, 10H, arom.), 7.93 (m, 2H, arom.), 10.54 (s, 2H, -OH).

2b: yellow crystalline solid. M.p: 234°C. IR (KBr, cm^{-1}): $\nu = 3202, 3437$. ^{1}HNMR ($CDCl_3$, ppm): $\delta = 4.05$ (s, 6H, $COOCH_3$), 7.19–7.39 (m, 6H, arom.), 7.85 (m, 2H, arom.), 8.67 (s, 2H, arom.), 10.66 (s, 2H, -OH). Anal. calc. For $C_{24}H_{18}O_6$: C 71.54, H 4.45. Found C 71.62, H 4.51.

3b: yellowish crystalline solid. M.p: 181°C (lit. (7): 182–183°C). IR (KBr, cm^{-1}): $\nu = 3258, 3433$. ^{1}HNMR ($CDCl_3$, ppm): $\delta = 4.08$ (s, 3H, $COOCH_3$), 4.99 (s, 1H, -OH), 7.25–7.40 (m, 7H, arom.), 7.87–7.99 (m, 3H, arom.), 8.78 (s, 1H, arom.), 10.81 (s, 1H, -OH).

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