Pergamon

Tetrahedron Letters, Vol. 35, No. 29, pp. 5217-5220, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01021-8

Regioselective Electrocatalyzed $S_{RN}1$ Reactions with 2-*tert*-Butyl-1-naphthol.

C. Combellas, C. Suba, A. Thiébault

Laboratoire de Chimie et Electrochimie des Matériaux Moléculaires
ESPCI, 10, rue Vauquelin, 75231 Paris Cedex 05, France

Key Words: $S_{RN}1$; 1-naphthol; 2-*tert*-butyl-1-naphthol; 4-aryl-2-*tert*-butyl-1-naphthols.

Abstract: *4-aryl-2-tert-butyl-1-naphthols are obtained regioselectively from 2-tert-butyl-1-napthol by an electro-induced $S_{RN}1$ reaction in liquid ammonia. The reaction is illustrated with different aryl chlorides as starting compounds (aryl= pyridyl, quinolinyl, phenylpyridine); the yields are between 60 and 85%. The tert-butyl substituent can be further eliminated by a trans-alkylation reaction.*

$S_{RN}1$ reactions make possible the formation of bonds between an aryl moiety and elements from the IVA (C, Si,..), VA (P, Sn,..), VIA (S, Se, Te,..) periods.[1] Phenoxides and naphthoxides can be used as nucleophiles in such reactions to create C-C bonds between different aryl moieties.[2-13] The reactions of phenoxide[2,3] or 1-naphthoxide[4,5] lead to mixtures of isomers coupled on positions 2 and 4. With 2-naphthoxide[6-9] and 2,6-di-*tert*-butyl phenoxide[10-13], the reaction is regioselective leading to 1 and 4 coupled products respectively.

We report here the regioselective coupling of 2-*tert*-butyl-1-naphthol with aromatic chlorides by an electro-induced $S_{RN}1$ reaction and the subsequent elimination of the 2-*tert*-butyl protecting group.

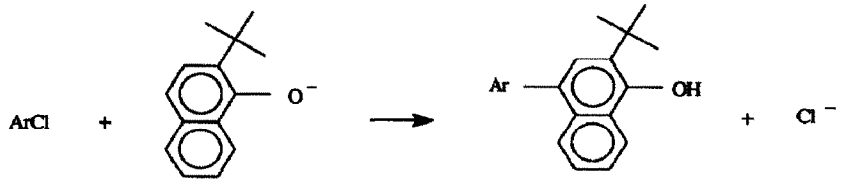
In a preliminary experiment, 1-naphthoxide was reacted with 4-chloropyridine under $S_{RN}1$ conditions, by way of a previously described method.[10] Two products were obtained, which could not be completely purified by flash chromatography. One of them could be identified as resulting from the coupling on position *para* to the hydroxyl group. The other one was evidenced (GC/MS) to be an isomer of the preceding one and assumed to be coupled on *ortho* to the hydroxyl group by analogy with literature data[4,5]. The yields of the two isomers were determined by GC (*ortho*:32%; *para*:41%).

Since *para*-substituted phenols are interesting compounds for nonlinear optics purposes, whilst *ortho*-substituted phenols are not[14], we have tried to synthesize regioselectively *para*-substituted naphthols, which should be efficient products for nonlinear optics. Because of the difficulties encountered in the separation of the regio isomers obtained, an alternative route to substituted 1-naphthoxides was investigated involving protection of one of the coupling positions of 1-naphthoxide. This protection at the *ortho*-position was performed with a *tert*-butyl group by a Friedel-Crafts reaction.[15]

The electro-induced $S_{RN}1$ reaction of 2-*tert*-butyl-1-naphthoxide with different aromatic chlorides ArX was carried out in liquid ammonia under the previously used conditions for 1-naphthoxide (aromatic halide: 5 mmol, 2-*tert*-butyl-1-naphthoxide: 15 mmol)[10], with indirect induction by the reduced form of a mediator

(2 mmol) selected so that its standard potential was about 400 mV more positive than that of the aromatic halide. With mediators such as 2,4' or 4,4'-bipyridine and quinoxaline, the reaction has to be performed in the presence of an additional base (potassium hydroxide, 5 mmol) in order to avoid the protonation of the reduced form of the mediator.

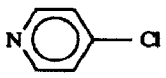
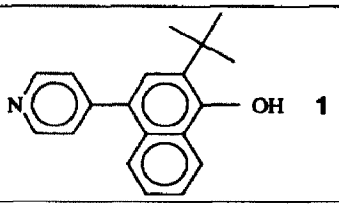
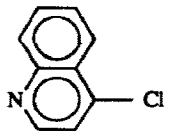
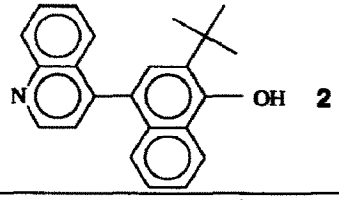
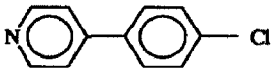
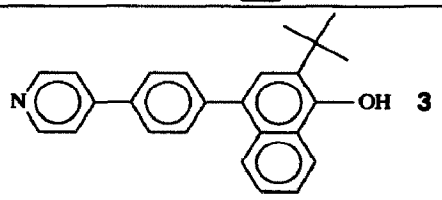
The overall reaction was the following (Scheme I) and the results are reported in Table I:



Scheme 1

Table I

Results of the Electrolyses with 2-*tert*-butyl-1-naphthoxide.[a]

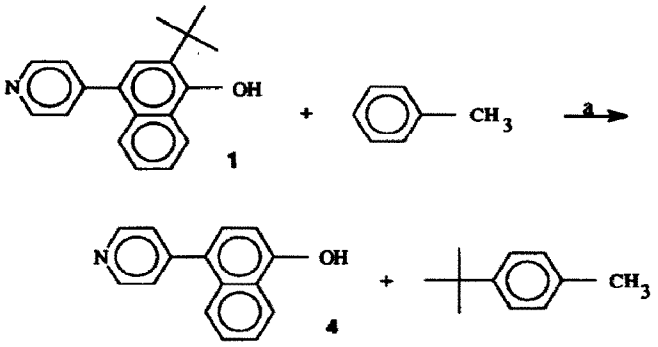
Starting compound	Mediator	Product	Yield[b]
	2,4'-bipyridine	 **1**	80 %
	quinoxaline	 **2**	85 %
 [c]	4,4'-bipyridine	 **3**	57 %

[a] intensiostatic conditions (0.5 A.dm^{-2}); charge consumed less than 1F per mole of consumed ArX, in good agreement with the yields obtained.

[b] isolated product.

[c] prepared by a cross-coupling reaction catalyzed by palladium according to literature procedure.[16]

In a model experiment (Scheme 2), removal of the *tert*-butyl group from the coupled product was achieved in yield of the same order as those found with phenoxides substituted by *tert*-butyl groups[12,17] (80%) by a *trans*-alkylation reaction using trifluoromethanesulfonic acid as catalyst[12,17]:



[a] 1 (0.425 mmol); CF_3SO_3H(1.58 mmol); 110°C; 4 hours.

Scheme 2

In summary, 2-*tert*-Butyl-1-naphthol makes possible the regioselective $S_{RN}1$ reaction with various hetaryl chlorides, which constitutes an important amelioration compared with the unprotected nucleophile. The *tert*-butyl group can be eliminated from the coupled products by a *trans*-alkylation reaction leading to the desired biaryl compounds in pure form.

Acknowledgements: This work was supported by DRET (contrat n° 93- 1087) which is gratefully acknowledged.

References and notes

(1) Rossi R. A.; Rossi R. H.; *Aromatic Substitution by the $S_{RN}1$ Mechanism*, American Chemical Society, Washington D C ACS Monograph 178, **1983**.

(2) Amatore C.; Combellas C.; Pinson J.; Savéant J.M.; Thiébault A.; *J. Chem. Soc., Chem. Commun.* **1988**, 7-8.

(3) Alam N.; Amatore C.; Combellas C.; Pinson J.; Savéant J.M.; Thiébault A.; *J. Org. Chem.* **1988**, *53*, 1496-1504.

(4) Beugelmans R.; Bois-Choussy M.; *Tetrahedron Lett.* **1988**, *29*, 1289-1292.

(5) Beugelmans R.; Bois-Choussy M.; Tang T.; *Tetrahedron Lett.* **1988**, *29*, 1705-1708.

(6) Beugelmans R.; Chastanet J.; *Tetrahedron Lett.* **1991**, *32*, 3487-3490.

(7) Beugelmans R.; Bois-Choussy M.; *J. Org. Chem.* **1991**, *56*, 2518-2522.

(8) Pierini A. B.; Baumgartner H. T.; Rossi R. A.; *J. Org. Chem* **1991**, *56*, 580-586.

(9) Beugelmans R.; Chastanet J.; *Tetrahedron* **1993**, *49*, 7883-7890.

(10) Alam N.; Amatore C.; Combellas C.; Thiébault A.; Verpeaux J.N.; *J. Org. Chem.* **1990**, *55*, 6347-6356.

(11) Boy P.; Combellas C.; Fielding S.; Thiébault A.; *Tetrahedron Let.* **1991**, *32*, 6705-6708.

(12) Boy P.; Combellas C.; Thiébault A.; *Synlett* **1991**, 923-924.

(13) Boy P.; Combellas C.; Thiébault A.; Amatore C.; A. Jutand; *Tetrahedron Let.* **1992**, *33*, 491-494.

(14) Barzoukas M.; Boy P.; Combellas C.; Fort A.; Thiébault A.; *Chem. Phys. Lett.* **1994**,00.

(15) Hirashima T.; Miyata T.; *Yuki Gosei Kagaku Kyokai Shi* **1976**, *34*, 433; Chem. Abstr. **1977**, 86, 171123x.

(16) Amatore C.; Jutand A.; Negri S.; Fauvarque J.F.; *J. Organometallic Chem.* **1990**, *390*, 389-398.

(17) Boy P.; Combellas C.; Suba C.; Thiébault A.; *J. Org. Chem.* **1994**,00.

Products analyses:

2-*tert*-butyl-4-(4-pyridyl)-1-naphthol (1)

mp= 295°C (dec); ^{1}H NMR (300 MHz, acetone D_6), δ (ppm)= 1.50 (s, 9H), 7.39 (s, H), 7.50 (d, J= 6 Hz, 2H), 7.42 to 7.56 (m, 2H), 7.77 (dd, J_1= 8 Hz, J_2= 1 Hz, H),8.33 (d, J= 8 Hz, H), 8.67 (d, J= 6 Hz, 2H), 9.50 (br. s, 1 naphtholic H); MS (EI), m/z= 277, 262; Anal. Calcd. for $C_{19}H_{19}NO$: C, 82.28; H, 6.90, N, 5.05; Found: C, 82.24; H, 6.96, N, 5.01.

2-*tert*-butyl-4-(4-quinolinyl)-1-naphthol (2)

mp= 291°C (dec); ^{1}H NMR (300 MHz, acetone D_6), δ (ppm)= 1.57 (s, 9H), 7.28 (dd, J_1= 8 Hz, J_2= 1 Hz, H), 7.31 (dd, J_1= 8 Hz, J_2= 1 Hz, H), 7.43 (dd, J_1= 4 Hz, J_2= 1 Hz, 2H), 7.49 (d, J= 4 Hz, H), 7.50 to 7.53 (m, H), 7.53 (s, H), 7.53 (dt, J_1= 8 Hz, J_2= 4 Hz, H), 8.16 (d, J= 8.5 Hz, H), 8.42 (d, J= 8.5 Hz, H), 8.48 (s, 1 naphtholic H), 9.01 (d, J= 4 Hz, H); MS (EI), m/z= 327, 312; Anal. Calcd. for $C_{23}H_{21}NO$: C, 84.37; H, 6.46, N, 4.28; Found: C, 83.38; H, 6.43, N, 4.12.

2-*tert*-butyl-4-[4-(4-pyridylphenyl)]-1-naphthol (3)

mp= 265°C (dec); ^{1}H NMR (300 MHz, DMSO D_6), δ (ppm)= 1.48 (s, 9H), 7.37 to 7.55 (m, 3H), 7.61 and 7.94 (AA'BB', J= 8 Hz, 4H), 7.76 to 7.85 (m, 3H), 8.32 (d, J= 8 Hz, H), 8.68 (d, J= 6 Hz, 2H), 9.36 (br s, 1 naphtholic H); MS (GC/MS), m/z= 353, 338; Anal. Calcd. for $C_{25}H_{23}NO$: C, 84.95; H, 6.59, N, 3.96; Found: C, 84.95; H, 6.68, N, 3.83.

4-(4-pyridyl)-1-naphthol (4)

mp=209°C; ^{1}H NMR (300 MHz, acetone D_6), δ (ppm)= 7.04 (d, J= 8 Hz, H), 7.33 (d, J= 8 Hz, H), 7.47 (d, J= 6 Hz, 2H), 7.45 to 7.68 (m, 2H), 7.82 to 7.90 (m, H), 8.33 to 8.42 (m, H), 8.69 (d, J= 6 Hz, 2H), 9.56 (br s, 1 naphtholic H); ^{13}C NMR (75.5 MHz, acetone D_6), δ (ppm)= 108.64 (CH), 123.58 (2 CH), 125.53 (C), 125.81 (CH), 125.93 (CH), 126.04 (CH), 127.80 (CH), 128.60 (CH), 129.53 (C), 132.77 (C), 149.57 (CH), 150.63 (2 CH), 154.75 (C); MS (GC/MS), m/z= 221; Anal. Calcd. for $C_{15}H_{11}O$: C, 81.43; H, 5.01, N, 6.33; Found: C, 81.35; H, 5.04, N, 6.21.

(*Received in France* 4 *May* 1994; *accepted* 25 *May* 1994)