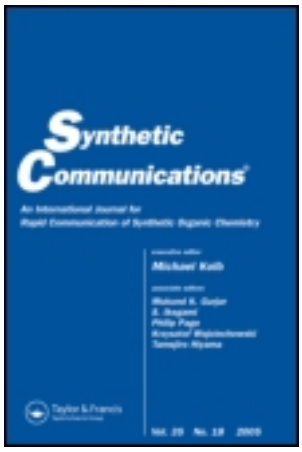


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

SYNTHESIS OF AMINONAPHTHALENE DERIVATIVES USING THE BUCHERER REACTION UNDER MICROWAVE IRRADIATION

Alvaro Cañete [a], Mónica X. Meléndrez [a], Claudio Saitz [a] & Antonio L. Zanocco [b]

[a] Department of Organic Chemistry and Physical Chemistry, Faculty of Chemical and Pharmaceutical Sciences, University of Chile, Casilla 233, Santiago 1, Chile

[b] Department of Organic Chemistry and Physical Chemistry, Faculty of Chemical and Pharmaceutical Sciences, University of Chile, Casilla 233, Santiago 1, Chile

Available online: 09 Nov 2006

To cite this article: Alvaro Cañete, Mónica X. Meléndrez, Claudio Saitz & Antonio L. Zanocco (2001): SYNTHESIS OF AMINONAPHTHALENE DERIVATIVES USING THE BUCHERER REACTION UNDER MICROWAVE IRRADIATION, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:14, 2143-2148

To link to this article: http://dx.doi.org/10.1081/SCC-100104465

SYNTHETIC COMMUNICATIONS, 31(14), 2143–2148 (2001)

SYNTHESIS OF AMINONAPHTHALENE DERIVATIVES USING THE BUCHERER REACTION UNDER MICROWAVE IRRADIATION

Alvaro Cañete, Mónica X. Meléndrez, Claudio Saitz, and Antonio L. Zanocco*

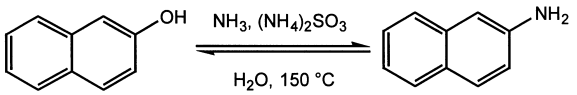
Department of Organic Chemistry and Physical Chemistry,
Faculty of Chemical and Pharmaceutical Sciences,
University of Chile, Casilla 233, Santiago 1, Chile

ABSTRACT

A very simple and efficient method to prepare aminonaphthalene derivatives in good yield using the Bucherer reaction under microwave irradiation in a closed vessel is described. A reaction time of 30 min at 150 Watts of microwave power was established as the optimum irradiation conditions when approximately 2 g of the initial hydroxynaphthalene was used in the synthesis.

In our studies related to the synthesis and evaluation of the photophysical and photochemical behavior of aryloxazinones we need several aminonaphthalene compounds which are intermediates in the synthesis of substituted naphthoxazinones. The Bucherer reaction (Eq. 1) provides a relatively simple method to synthesize primary, secondary and tertiary aromatic amines from hydroxyaromatic compounds or to obtain hydroxy

* Corresponding author. Fax: 56-2-6782822; E-mail: azanocco@ll.ciq.uchile.cl



(1)

compounds from aromatic amines.[1–4] It proceeds in the aqueous media with the presence of sulfurous acid or its salts and has been used to prepare several naphthalene derivatives in dye synthesis. However, Bucherer reaction involves the use of high pressure reactors and largest reaction times to obtain secondary or tertiary aminonaphthalenes in appropriate yields.[1]

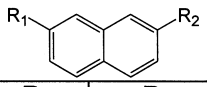
Otherwise, microwave assisted organic reactions have experienced an exponential growth in the last years. Microwave heating employing domestic or laboratory ovens has been used in many organic transformations as pericyclic reactions, rearrangements, oxidations, cyclization reactions, radical reactions, alkene synthesis, decarboxylations, etc.[5–8] However, the use of microwave technology has not been described in relation to the Bucherer reaction. Herein we wish to report the synthesis of naphthylamines under microwave irradiation. Also, an example of the utility of this method to obtain N,N-disubstituted anilines is included.

RESULTS AND DISCUSSION

Microwave irradiation by 30 min at 150 Watts of power of a mixture of β-naphthol, dimethylamine and dimethylammonium sulfite yields over 90% of N,N-dimethyl-2-naphthylamine. Using the same method, we obtain eight aminonaphthalene derivatives in yields between 70–90% that give satisfactory spectroscopic and analytical data. The results are summarized in Table 1. N,N,N′,N′-tetramethyl-2,7-naphthalenediamine was obtained from 2,7-dihydroxynaphthalene employing a large excess (1:8 molar ratio) of aqueous dimethylamine. To determine the optimum reaction-time for this synthetic procedure we observed the effect of both the applied microwave power and the irradiation time on the yield of the reaction between of β-naphthol and dimethylamine. As can be seen in Figure 1, at 250 Watts and an additional 15 min of irradiation, the best product yields are 85%. Not better results could be obtained under these conditions, probably due to partial decomposition of the aminonaphthalene because of a temperature raise to $>200^{\circ}$C. At 150 and 80 Watts yields increase linearly with the irradiation time. From these results, 30 min at 150 Watts was established as the optimum reaction time when approximately 2 g of hydroxynaphthalene was used. In conclusion, our experimental procedure provides a very simple and efficient way to obtain aminonaphthalene derivatives in good yield and short reaction times.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Table 1. Synthesis of Aminonaphthalene Derivatives by Using the Bucherer Reaction Under Microwave Irradiation

Reagents		Product 		Yield (%)
Hydroxy aromatic	Amine	R_1	R_2	
2-Naphtol	Ammonia	H	NH_2	93
2-Naphtol	Dimethylamine	H	$N(CH_3)_2$	90
2-Naphtol	Diisopropylamine	H	$N(i\text{-}Prop)_2$	70
2-Naphtol	Aniline	H	NH-ϕ	68
7-Methoxy-2-naphtol	Dimethylamine	$N(CH_3)_2$	OCH_3	94
2,7-Dihydroxynaphthalene	Dimethylamine	$N(CH_3)_2$	$N(CH_3)_2$	95
2,7-Dihydroxynaphthalene	Dimethylamine	$N(CH_3)_2$	OH	66
7-Methoxy-2-naphtol	Ammonia	OCH_3	NH_2	88
Phenol	Dibutylamine	N,N-Dibutylaniline		90

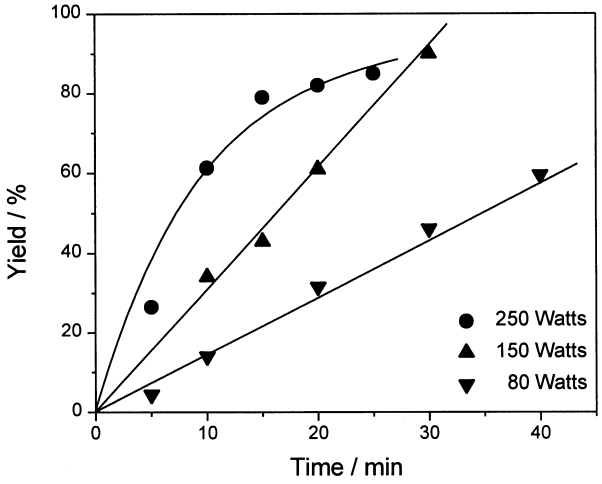


Figure 1. Dependence of the yield for the reaction between of β-naphthol and dimethylamine on the irradiation time at different applied microwave power.

EXPERIMENTAL

All commercially available reagents 2,7-dihydroxynaphthalene, 2-hydroxy-7-methoxynaphthalene, β-naphthol, phenol, diisopropylamine, dibutylamine, aniline (Aldrich), aqueous ammonia and 40% aqueous dimethylamine (Merck) were used as received from the suppliers.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

NMR spectra were performed in a Bruker DRX-300 spectrometer. Chemical shifts are given part per million positive values down field from internal tetramethylsilane, TMS, standard. Melting points were obtained in a modified Koffler apparatus and were uncorrected. The elemental analyses were performed in a Fisons EA-1108 instrument. Microwave assisted reactions were carried out using a Milestone microwave oven model MLS-1200 MEGA of variable radiofrequency.

General Procedure for the Microwave Assisted Bucherer Reaction

Typically, 2 g of the hydroxyaromatic compound, 0.024 mol of amine and 10 to 12 ml of a freshly prepared aqueous solution of 0.024 mol of amine (equivalent quantities of aqueous ammonia or 40% aqueous dimethylamine were used in the synthesis of amine or dimethylamine derivatives, respectively) saturated with sulfur dioxide were introduced in a sealed poly(tetrafluoroethylene) acid digestion vessel and microwave irradiated during 30 min at 150 Watts (23% of energy efficiency). After irradiation was stopped, the vessel was cooled to ambient temperature in a water bath. Then, the solid product was filtered, washed with alkaline water and dissolved in methylene dichloride. The organic solution was washed with NaOH 0.1 M, dried over anhydrous Na_2SO_4, the solvent was removed and the crude product was purified by recrystallization or distillation.

2-Naphthylamine. Yield = 93%, m.p. = 109–110°C (113).[9] Elemental anal. calcd. for $C_{10}H_9N$: C, 83.88; H, 6.34; N, 9.78; found: C, 83.92; H, 6.06; N, 9.52. ^{1}H-NMR ($CDCl_3$) δ: 3.72 (s, 2H, NH_2); 6.92 (m, 2H, H1, H3); 7.18 (t, 1H, J = 6.82 Hz, H6); 7.32 (t, 1H, J = 6.82 Hz, H7); 7.45 (d, 1H, J = 8.19 Hz, H5); 7.64 (d, 2H, J = 6.82 Hz, H4, H8). ^{13}C-NMR ($CDCl_3$) δ: 143.96, 134.86, 129.17, 127.95, 127.67, 126.31, 125.77, 122.46, 118.21, 108.66.

N,N-Dimethyl-2-naphthylamine. Yield = 90%, m.p. = 50–51°C (52–53).[9] Elemental anal. calcd. for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18; found: C, 84.02; H, 7.55; N, 8.22. ^{1}H-NMR ($CDCl_3$) δ: 3.15 (s, 6H, CH_3); 7.05 (d, 1H, J = 2.5 Hz, H1); 7.28 (d, 1H, J = 9.11 Hz, H3); 7.31 (t, 1H, J = 7.39 Hz, H6); 7.48 (t, 1H, J = 7.55 Hz, H7); 7.80 (m, 3H, H5, H4, H8). ^{13}C-NMR ($CDCl_3$) δ: 148.61, 134.94, 128.66, 127.41, 126.89, 126.17, 122.07, 116.46, 106.57, 40.91 (CH_3).

N,N-Diisopropyl-2-naphthylamine. Yield = 70%, m.p. = 72–73°C. Elemental anal. calcd. for $C_{16}H_{21}N$: C, 84.53; H, 9.31; N, 6.16; found; C, 84.12; H, 9.25; N, 6.22. ^{1}H-NMR ($CDCl_3$) δ: 1.19 (d, 6H, J = 6.39 Hz, CH_3); 3.67 (m, 1H, CH); 6.80 (m, 2H, H1, H3); 7.11 (t, 1H, J = 7.06 Hz, H6); 7.27 (t, 1H, J = 7.78 Hz, H7); 7.56 (m, 3H, H4, H5, H8). ^{13}C-NMR

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

($CDCl_3$) δ: 146.52, 134.86, 128.60, 127.15, 126.52, 126.03, 122.12, 116.23, 106.02, 60.41 (N-CH), 24.16 (CH_3).

N-Phenyl-2-naphthylamine. Yield = 68%, m.p. = 98–101 °C (108).[9] Elemental anal. calcd. for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39; found: C, 87.42; H, 5.69; N, 6.31. ^{1}H-NMR ($CDCl_3$) δ: 4.02 (s, 1H, NH); 6.70 (d, 2H, J = 7.66 Hz, Ho); 6.78 (t, 1H, J = 7.37 Hz, Hp); 7.05 (d, 1H, J = 2.49 Hz, H1); 7.08 (d, 1H, J = 8.37 Hz, H3); 7.16 (t, 2H, J = 7.83 Hz, Hm); 7.31 (t, 1H, J = 8.02 Hz, H6); 7.41 (t, 1H, J = 7.94 Hz, H8); 7.64 (d, 1H, J = 7.94 Hz, H5); 7.74 (m, 2H, H4, H8). ^{13}C-NMR ($CDCl_3$) δ: 153.40, 145.92, 134.56, 129.75, 129.29, 128.84, 127.70, 126.43, 126.30, 123.50, 118.92, 117.77, 115.38, 109.45.

2-Methoxy-7-N,N-dimethylnaphthylamine. Yield = 94%, m.p. = 69–70°C. Elemental anal. calcd. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96; O, 7.95; found: C, 77.32; H, 7.25; N, 6.92. ^{1}H-NMR ($CDCl_3$) δ: 3.01 (s, 6H, N-$(CH_3)_2$); 3.86 (s, 3H, O-CH_3); 6.84 (m, 2H, H1, H8); 6.97 (m, 2H, H3, H6); 7.55 (d, 1H, J = 9.96 Hz, H5); 7.59 (d, 1H, J = 9.25 Hz, H4). ^{13}C-NMR ($CDCl_3$) δ: 158.72, 150.23, 136.12, 129.45, 129.23, 124.63, 116.54, 115.46, 108.96, 104.75, 55.25, 40.65.

N,N,N′,N′-Tetramethyl-2,7-naphthalenediamine. Yield = 95%, m.p. = 38–39 (40).[10] Elemental anal. calcd. for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07; found: C, 78.32; H, 8.58; N, 13.06. ^{1}H-NMR ($CDCl_3$) δ: 3.07 (s, 12H, CH_3); 6.84 (d, 2H, J = 2.34 Hz, H1, H8); 6.95 (dd, 2H, J = 8.93 Hz, H3, H6); 7.59 (d, 2H, J = 8.93 Hz, H4, H5) ^{13}C-NMR ($CDCI_3$) δ:. 149.14, 136.35, 128.22, 120.62, 112.98, 105.50, 40.99 (N-CH_3).

7-N,N-Dimethylamino-2-naphthol. Yield = 66%, m.p. = 130–131°C. Elemental anal. calcd. for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48; O, 8.54; found: C, 76.83; H, 6.95; N, 7.23. ^{1}H-NMR ($CDCl_3$) δ: 3.07 (s, 6H, N-CH_3); 5.25 (s, 1H, O-H); 6.78 (d, 1H, J = 2.42 Hz, H8), 6.84 (dd, 1H, J = 8.70 Hz, J = 2.90 Hz, H3); 6.95 (d, 1H, J = 2.90 Hz, H1); 7.03 (dd, 1H, J = 9.02 Hz, J = 2.42 Hz, H6); 7.51 (d, 1H, J = 8.78 Hz, H5); 7.55 (d, 1H, J = 9.12 Hz, H4). ^{13}C-NMR ($CDCl_3$) δ: 154.07, 149.13, 136.20, 129.35, 128.56, 115.34, 114.14, 113.71, 107.96, 105.20, 40.84 (N-CH_3).

7-Methoxy-2-naphthylamine. Yield = 88%, m.p. = 138−139°C (143).[11] Elemental anal. calcd. for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09; O, 9.24; found: C, 75.99; H, 6.27; N, 8.11. ^{1}H-NMR ($CDCl_3$) δ: 3.78 (s, 2H, N-H_2); 3.85 (s, 3H, O-CH_3); 6.75 (dd, 1H, J = 8.61 Hz, H3); 6.85 (m, 3H, H1, H6, H8); 7.53 (m, 2H, H4, H5). ^{13}C-NMR ($CDCl_3$) δ: 158.20, 144.20, 135.95, 129.55, 129.25, 124.33, 116.21, 115.21, 108.82, 104.68, 55.23 (O-CH_3).

N,N-Dibutylaniline. Yield = 90%, b.p. 160°C (4 mm Hg) (269 (760 mm Hg)). Elemental anal. calcd. for $C_{14}H_{23}N$: C, 81.89; H, 11.29; N, 6.82; found: C, 81.70; H, 11.09; N, 7.04. ^{1}H-NMR ($CDCl_3$) δ: 0.97 (m, 6H, C-CH_3); 1.32 (m, 4H, C-H^3); 1.66 (m, 4H, C-H^2); 2.74 (m, 4H, C-H^1);

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

6.90 (d, 2H, J = 8.82 Hz, Ho), 7.24 (m, 3H, Hm, Hp). ^{13}C-NMR ($CDCl_3$) δ: 144.84, 129.37, 119.42, 115.67, 47.54, 27.92, 19.83, 13.41 (CH_3).

ACKNOWLEDGMENTS

The facilities provided by CEPEDEQ, Universidad de Chile are gratefully acknowledged.

REFERENCES

1. Seeboth, H. Angew. Chem. Int. Ed. Engl. **1967**, *6*, 308.
2. Drake, N.L. Org. Reactions **1942**, *1*, 105.
3. Rieche, A. and Seeboth, H. Liebigs Ann. Chem. **1960**, *638*, 66.
4. Seeboth, H. and Rieche, A. Liebigs Ann. Chem. **1964**, *671*, 77.
5. Majetich, G. and Hicks, R.J. Microwave Power E. E. **1995**, *30*, 27.
6. Strauss, C.R. and Trainor, R.W. Aus. J. Chem. **1995**, *48*, 1665.
7. Caddick, S. Tetrahedron **1995**, *51*, 38.
8. Michael, D.; Mingos, P. and Baghurst, D.R. Chem. Soc. Rev. **1991**, *20*, 1.
9. *CRC Handbook of Chemistry and Physics*, David R. Lide Ed., 73rd Ed., CRC Press, Boca Raton, 1993.
10. Zweig, A.; Maurer, A.H. and Roberts, B.G. J. Org. Chem. **1966**, *32*, 1322.
11. Windaus, A. Ber. **1924**, *57B*, 1731.

Received in the USA October 12, 2000