Asian Journal of Chemistry; *Vol. 23, No. 10 (2011), 4713-4714*

ASIAN JOURNAL OF CHEMISTRY

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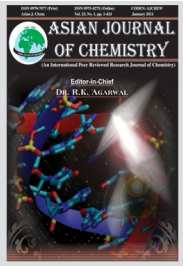

NOTE

Solvent-Free Synthesis of 1,8-Naphthalimide Derivatives Under Microwaves Irradiation

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(*Received*: 5 February 2011; *Accepted*: 1 July 2011) AJC-10140

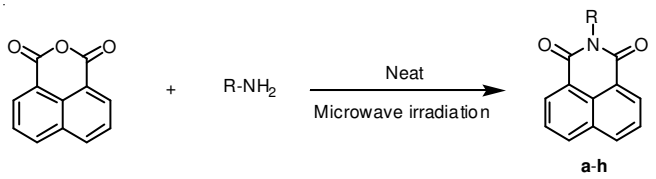
A solvent-free synthesis of a series of 1,8-naphthalimide derivatives, which proceeds *via* facile, economical and efficient reaction of primary amine with 1,8-naphthalic anhydride derivatives under microwave irradiation, was described.

Key Words: Naphthalimide, Solvent-free, Microwave.

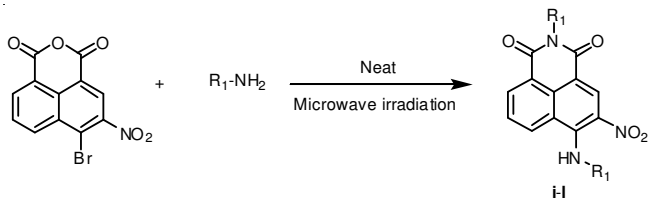
Solvent-free organic reactions have aroused great interest, particularly from the standpoint of green chemistry, because harmful organic solvents are not contained in the production process[1,2]. Solvent-free organic reactions are frequently carried out in combination with microwave irradiation, since that microwave irradiation[3] is regarded as a green technology and its level of energy consumption is lower compared with traditional methods.

Recently, numerous efforts have been taken to the synthesis of 1,8-naphthalimide derivatives, because they have been widely used as textile materials[3], fluorescent tags[4], and DNA-photocleavers[5] *etc*. Available synthetic methods for naphthalimides are listed in literature[6-10]. However, most of these routes are environmentally harmful and require long reaction time and a large excess of organic solvents as the reaction medium or even complicated work-up steps after reaction[6-10]. Thus, preparation of functionalized 1,8-naphtalimide derivatives require more improvement. Here we report a method for the preparation of 1,8-naphthalimides in good yields using microwave irradiation (**Schemes I** and **II**). To our best of knowledge, this method has not been mentioned previously in literature and it is simple and useful.

Solvent-free synthesis of 1,8-naphtalimide derivatives was done in Galanz G80F20CN2L-B8 microwave oven. The mixture of primary amine and 1,8-naphthalic anhydride or 3-nitro-4-bromo-1,8-naphthalic anhydride was blended together and reacted at 400-800 watt in an unmodified household microwave oven with intermittent heating for a few minutes, respectively. After reaction, the gum obtained was recrystallized with ethanol and dimethyl fomamide. Upon recrystallization, white crystals



Scheme-I



Scheme-II

of **a-h** and red crystals of **i-l** were obtained. It can be seen that the work-up after reaction was very simple. In addition, conventional heating method was also used for comparison and the mixture of primary amine and 1,8-anhydride naphthalene or 3-nitro-4-bromo-1,8-naphthalic anhydride was refluxed in ethanol and DMF, respectively (Table-1).

As seen in Table-1, the yields in the two methods were almost the same. However, the reaction time was about 4-7 h in the conventional heating method, while the reaction time was shortened to a few minutes under the solvent-free and microwave irradiation conditions. Therefore, the procedure under the solvent-free and microwave irradiation conditions has the advantages of good yield, short reaction time, environmental benign and easy work-up.

TABLE-1
OPTIMIZATION OF REACTION CONDITIONS FOR PREPARATION OF 1,8-NAPHTHALIMIDES USING MICROWAVES

Reactant	Amine* (mmol)	Product	Power (watt)	Time (min)	Yield$^{\alpha}$ (%)	Yield$^{\beta}$ (%) (time h)
Aniline	0.4	**a**	640	5.5	91	78 (6)
Benzylamine	0.4	**b**	640	4.0	95	74 (4)
o-Toluidine	0.4	**c**	640	5.0	89	87 (6)
Ethanolamine	0.4	**d**	640	3.0	98	84 (4)
3-Dimethylamino-1-propylamine	0.4	**e**	640	5.0	81	75 (6)
Butylamine	0.4	**f**	480	6.0	78	69 (6)
sec-Butylamine	0.4	**g**	480	6.0	71	75 (6)
Propylamine	0.6	**h**	480	7.0	75	81 (6)
Benzylamine	0.4	**i**	800	15.0	87	88(6)
Ethanolamine	0.4	**j**	800	12.0	94	95(6)
Butylamine	0.8	**k**	560	15.0	81	88(7)
Propylamine	0.8	**l**	560	15.0	84	87(7)

α: Using MW at power 400-800 W. α: Using conventional heating method: refluxed in organic solvents. *Both of the quantity of 1,8-naphthalic anhydride and 3-nitro-4-bromo-1,8-naphthalic anhydride are 0.1 mmol.

Characterization data of representative compounds

Compound c: m.p. 221.5-222.9 ºC. Anal. calcd. (%) for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56, N, 4.88. Found (%): C, 79.51; H, 4.67; N, 4.73. MS (ESI) m/z: 288 $[M]^+$. IR (KBr, ν_{max}, cm^{-1}): 3443, 3061, 2917, 1702, 1672, 1660, 1627, 1604, 1587; ^1H NMR (500 MHz, $CDCl_3$) δ: 8.68 (d, *J* = 7.6 Hz, 2H), 8.32 (d, *J* = 7.9 Hz, 2H), 7.84 (t, *J* = 7.8 Hz, 2H), 7.43 (m, *J* = 4.3 Hz, 3H), 7.24 (s, 1H), 2.21 (s, 3H).

Compound e: m.p. 60-61.3 ºC. Anal. calcd. (%) for $C_{17}H_{18}N_2O_2$: C, 73.32; H, 6.43; N, 9.92. Found (%): C, 73.01; H, 6.74; N, 9.85. MS (ESI) m/z: 283 $[M]^+$. IR (KBr, ν_{max}, cm^{-1}): 3444, 3060, 2943, 2856, 2812, 2730, 27878, 2762, 1697, 1653, 1625, 1590. ^1H NMR (500 MHz, $CDCl_3$) δ: 8.64 (d, *J* = 7.5 Hz, 2H), 8.25 (d, *J* = 8.1 Hz, 2H), 7.78 (t, *J* = 7.8 Hz, 2H), 4.25 (t, *J* = 7.8 Hz, 2H), 2.47 (t, *J* = 7.4 Hz 2H), 2.28 (s, 6H), 1.97 (t, *J* = 7.3 Hz, 2H).

Compound g: m.p. 111.0-111.5 ºC. Anal. calcd. (%) for $C_{16}H_{15}NO_2$: C, 75.85; H, 5.97; N, 5.53. Found (%): C, 75.63; H, 5.66; N, 5.41. MS (ESI) m/z: 254 $[M]^+$. IR (KBr, ν_{max}, cm^{-1}): 3446, 3071, 2966, 2935, 2875, 1694, 1662, 1627, 1589. ^1H NMR (500 MHz, $CDCl_3$) δ: 8.60 (d, *J* = 7.4 Hz, 2H), 8.23 (d, *J* = 7.9 Hz, 2H), 7.78 (t, *J* = 7.8 Hz, 2H), 5.25 (m, 2H), 2.24 (m, 2H), 1.97 (m, 2H), 1.59 (t, *J* = 14.7 Hz, 3H), 0.95(t, *J* = 7.4 Hz, 3H).

Compound i: m.p. 233.5.4-234.7 ºC. Anal. calcd. (%) for $C_{26}H_{19}N_3O_4$: C, 71.39; H, 4.38; N, 9.61. Found (%): C, 71.25; H, 4.51; N, 9.72. MS (ESI) m/z: 436 (M^+ - 1). IR (KBr, ν_{max}, cm^{-1}): 3441, 3060, 2923, 2851, 1699, 1655, 1601, 1537; ^1H NMR (500 MHz, $CDCl_3$) δ 10.02 (s, 1H, NH), 9.36(s, 1H), 8.70 (d, *J* = 7.4 Hz, 1H), 8.63 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.26-7.65 (m, 10H), 5.38 (s, 2H), 5.10 (s, 2H).

Compound j: m.p. 241.4-243 ºC. Anal. calcd. (%) for $C_{16}H_{15}N_3O_6$: C, 55.65; H, 4.38; N, 12.17. Found (%): C, 55.51; H, 4.51; N, 12.35. MS (ESI) m/z: 344 (M^+ - 1). IR (KBr, ν_{max}, cm^{-1}): 3444, 3060, 2943, 2856, 2812, 2730, 27878, 2762, 1697, 1653, 1625, 1590; ^1H NMR (500 MHz, DMSO) δ 9.84 (s, 1H, NH), 8.78 (d, *J* = 8.5 Hz, 1H), 8.70 (s, 1H), 8.43 (d, *J* = 7.4 Hz, 1H), 7.72 (t, *J* = 7.9 Hz, 1H), 5.24 (t, *J* = 4.8 Hz, 1H), 4.78 (t, *J* = 6.0 Hz, 1H), 4.02 (t, *J* = 6.7 Hz, 2H), 3.86 (s, 2H, OH), 3.70-3.73 (dd, *J* = 4.9 and 4.9 Hz, 2H), 3.56 (m, 2H).

Compound k: m.p. 236.5.4-236.7 ºC. Anal. calcd. (%) for $C_{20}H_{19}N3O_4$: C, 65.03; H, 6.28; N, 11.37. Found (%): C, 65.16; H, 6.47; N, 11.24. MS (ESI) m/z: 368 (M^+ - 1). IR (KBr, ν_{max}, cm^{-1}): 3462, 3060, 2958, 2929, 2873, 1698, 1649, 1606, 1577, 1538; ^1H NMR (500 MHz, $CDCl_3$) δ 9.92 (s, 1H, NH), 9.32 (s, 1H), 8.68 (dd, *J* = 7.4 and 8.5 Hz, 2H), 7.71 (t, *J* = 7.8 Hz, 1H), 4.18 (t, *J* = 7.5 Hz, 2H), 3.99 (t, *J* = 5.5 Hz, 2H), 1.45-1.88 (m, 8H), 1.00 (s, 6H, CH_3).

Compound l: m.p. 224.3-225.9 ºC. Anal. calcd. (%) for $C_{18}H_{19}N_3O_4$: C, 66.33; H, 5.61; N, 12.31. Found (%): C, 66.19; H, 5.73; N, 12.42. MS (ESI) m/z: 340 (M^+ - 1). IR (KBr, ν_{max}, cm^{-1}): 3453, 2965, 2933, 2856, 2812, 1694, 1652, 1602, 1581, 1536; ^1H NMR (500 MHz, $CDCl_3$) δ 9.91 (s, 1H, NH), 9.25 (s, 1H), 8.65 (t, *J* = 7.1 Hz, 2H), 7.71 (t, *J* = 7.8 Hz, 1H), 4.18 (t, *J* = 7.5 Hz, 2H), 3.96 (t, *J* = 5.4 Hz, 2H), 1.73-1.91 (m, 4H), 1.03 (s, 6H, CH_3).

ACKNOWLEDGEMENTS

This study was supported by Guangxi Department of Education Research Project (No. 200807MS075, 200807-MS076, 200911MS281, 200911MS282).

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