

## Note

### Environmentally co-friendly thiolation of 1,4-naphthoquinone

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A rapid thiolation of 1,4-naphthoquinone at the C-2 position is reported using 2-mercapto-5-alkyl-1,3,4-oxadiazole/thiadiazole in dry media using neutral alumina as solid support under microwave irradiation.

The use of solid supports<sup>1,2</sup> as well as microwaves<sup>3-6</sup> is a well established pollution free technique currently under investigation by synthetic organic chemist. Keeping this in view it was thought worthwhile to do the thiolation of 1,4-naphthoquinone in dry media under microwave irradiation in order to develop a rapid, safe, economical and environmentally co-friendly method devoid of solvent usage.

The solvent free reactions<sup>7-8</sup> are especially appealing as they provide an opportunity to work with open vessels, thus avoiding the risk of high pressure development and with a possibility of carrying out the reaction on a preparative scale in addition to the associated selectivity. Microwave activation rather than conventional heating was

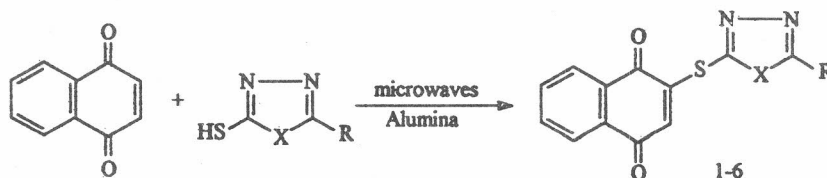
preferred as solid supports are rather poor thermal conductors (with consequently an important gradient in temperature inside the materials), whereas they behave as strong microwave absorbents (and therefore with a better homogeneity in temperatures<sup>9-10</sup>). Consequently reactions were generally faster and the products obtained were of high purity.<sup>10-11</sup>

### Results and Discussion

We report herein the thiolation of 1,4-naphthoquinone under microwave irradiation in dry media. The products formed are given in Scheme I and the results in Table I. 2-Mercapto-5-alkyl-1,3,4-oxadiazole/thiadiazole was synthesized according to literature method<sup>12</sup> which was then reacted with 1,4-naphthoquinone. In IR spectrum the absorption bands at 1675 and 1660  $\text{cm}^{-1}$  were observed due to C=O group and at 1530  $\text{cm}^{-1}$  due to C=N group. The peak at  $\delta$  13.2 (s, 1H, 2-SH) due to oxadiazoles/thiadiazoles in the PMR spectrum was absent confirming the formation of products 1-6.

### Experimental Section

Melting points (uncorrected) were recorded on an electrothermal apparatus. IR spectra ( $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ ) were recorded on 1710 Perkin Elmer Spectrophotometer using KBr discs and  $^1\text{H}$  NMR



R	R
1 C <sub>7</sub> H <sub>15</sub>	4 C <sub>7</sub> H <sub>15</sub>
X=O 2 C <sub>9</sub> H <sub>19</sub>	X=S 5 C <sub>9</sub> H <sub>19</sub>
3 C <sub>11</sub> H <sub>23</sub>	6 C <sub>11</sub> H <sub>23</sub>

Table I—Physical and spectral data					
Compd	mp °C	Yield (%)	M <sup>+</sup> observed (expected)	IR ( $\nu_{\max}$ in $\text{cm}^{-1}$ )	<sup>1</sup> H NMR (Acetone- <i>d</i> <sub>6</sub> )
1	75	75	356 (356)	1675, 1660 (C=O) 1530 (C=N)	0.9 (t, 3H, 7"-CH <sub>3</sub> ), 1.29 (m, 8H, 4×CH <sub>2</sub> ), 1.6 (m, 2H, 2"-CH <sub>2</sub> ), 2.35 (t, 2H, 1"-CH <sub>2</sub> ), 6.20 (s, 1H, 3C-H), 7.70-7.90 (m, 2H, Ar-H), 8.00-8.30 (m, 2H, Ar-H).
2	66	80	385 (384)	1670, 1655 (C=O) 1530 (C=N)	0.89 (t, 3H, 9"-CH <sub>3</sub> ), 1.27 (m, 12H, 6×CH <sub>2</sub> ), 1.62 (m, 2H, 2"-CH <sub>2</sub> ), 2.34 (t, 2H, 1"-CH <sub>2</sub> ), 6.10 (s, 1H, 3C-H), 7.75-7.90 (m, 2H, Ar-H), 8.1-8.30 (m, 2H, Ar-H)
3	110	68	410 (412)	1675, 1655 (C=O) 1560 (C=N)	0.89 (t, 3H, 11"-CH <sub>3</sub> ), 1.26 (m, 16H, 8×CH <sub>2</sub> ), 1.6 (m, 2H, 2"-CH <sub>2</sub> ), 2.34 (t, 2H, 1"-CH <sub>2</sub> ), 6.00 (s, 1H, 3C-H), 7.70-7.92 (m, 2H, Ar-H), 8.00-8.32 (m, 2H, Ar-H).
4	80	83	340 (340)	1670, 1660 (C=O) 1550 (C=N)	0.89 (t, 3H, 7"-CH <sub>3</sub> ), 1.28 (m, 8H, 4×CH <sub>2</sub> ), 1.6 (m, 2H, 2"-CH <sub>2</sub> ), 2.35 (t, 2H, 1"-CH <sub>2</sub> ), 6.20 (s, 1H, 3C-H), 7.70-7.90 (m, 2H, Ar-H), 8.06-8.36 (m, 2H, Ar-H).
5	150	85	368 (368)	1675, 1660 (C=O) 1540 (C=N)	0.88 (t, 3H, 9"-CH <sub>3</sub> ), 1.26 (m, 12H, 6×CH <sub>2</sub> ), 1.62 (m, 2H, 2"-CH <sub>2</sub> ), 2.3 (t, 2H, 1"-CH <sub>2</sub> ), 6.10 (s, 1H, 3C-H), 7.60-7.92 (m, 2H, Ar-H), 8.06-8.38 (m, 2H, Ar-H).
6	132	65	398 (396)	1680, 1655 (C=O) 1550 (C=N)	0.88 (t, 3H, 11"-CH <sub>3</sub> ), 1.27 (m, 16H, 8×CH <sub>2</sub> ), 1.61 (m, 2H, 2"-CH <sub>2</sub> ), 2.32 (t, 2H, 1"-CH <sub>2</sub> ), 6.00 (s, 1H, 3C-H), 7.60-7.84 (m, 2H, Ar-H), 8.1-8.40 (m, 2H, Ar-H).

on Hitachi R-600 FT spectrophotometer using Me<sub>4</sub>Si as internal standard (chemical shifts in  $\delta$ , ppm). The purity of compounds was checked by TLC on silica coated Al plates (Merck). All the sequences of irradiation were carried out in Padmini essentia microwave oven model Brownie using high as level of irradiation.

**Synthesis of 2-thio-[5'-alkyl-1',3',4'-thiadiazole / oxadiazole]-1,4-naphthoquinone.** 1,4-Naphthoquinone (1mmole) and 2-mercapto-5-alkyl-1,3,4-thiadiazole/oxadiazole (1mmole) was adsorbed on neutral alumina. The beaker containing the above material was irradiated inside the microwave oven for 2-5 min at 2450 MHz. The reaction mixture was cooled from 200°C to room temperature and eluted with acetone (3 × 10 mL). The elutant was evaporated to dryness to yield the product which was recrystallised from ethyl acetate-pet. ether (10-15 mL).

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