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Microwave-assisted selenium dioxide mediated selective oxidation of 1-tetralones to 1,2-naphthoquinones

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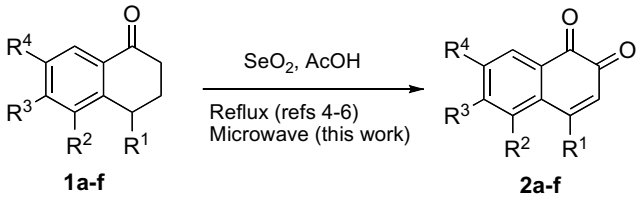
ABSTRACT

We report an improved procedure for the selective transformation of substituted 1-tetralones to 1,2-naphthoquinones by microwave-assisted selenium dioxide oxidation. The reaction time is effectively reduced from hours to seconds without any loss of yield (40–70%) or selectivity.

As part of our programme directed towards the total synthesis of steroids, we required access to variously substituted 1,2-naphthoquinones.[1] Of the methods available to synthesise 1,2-naphthoquinones,[2,3] the procedure of Kishi, modified by Bekaert, appeared an attractive approach.[4–6] Thus, selenium dioxide was reported to oxidise 1-tetralones in glacial acetic acid at 60–70 °C in 4–7 h providing 1,2-naphthoquinone products in good yields (Scheme 1, 60–70%). In our hands, the oxidation generally required longer reaction times and it was necessary to use finely ground selenium dioxide powder.

Recently, it was reported that the synthesis of 1,2-dicarbonyl compounds by selenium dioxide oxidation was greatly accelerated by closed-vessel microwave (CVMW) irradiation.[7,8] Even the difficult oxidation of camphor to its corresponding 1,2-diketone was greatly accelerated. Indeed, it was reported that the selenium was better converted into selenium black and purification was simplified. In this Letter, we report the extension of CVMW-assisted selenium dioxide oxidations to include the conversion of 1-tetralones to 1,2-naphthoquinones.

The temperature and microwave hold time were varied in order to optimise the conversion of 1-tetralone **1a** into 1,2-naphthoquinone **2a**. Only reactions in glacial acetic acid were successful. It was also found that very short hold times were required (Table 1, entry 6) and were superior as less decomposition was observed (Table 1, entry 2) than for longer hold times.



Scheme 1. Selective selenium dioxide oxidation of 1-tetralones to 1,2-naphthoquinones.

The generality of this new accelerated procedure was assessed by subjecting substituted 1-tetralones **1b–f** to our optimised conditions (Table 2). In all cases, the corresponding 1,2-naphthoquinones were successfully obtained, including the previously unreported 5,7-dimethyl-1,2-naphthoquinone. In each case, complete conversion of starting material was confirmed by ^{1}H NMR analysis of the crude reaction mixture. Simple filtration to remove the precipitated selenium gave a crude material of approximately 85–90% purity. Where higher purity material was required, the crude material was purified by flash chromatography. In these cases, this chromatography was accompanied by significant product decomposition.

In most cases, closed-vessel microwave irradiation greatly accelerates the selenium dioxide promoted conversion of tetralones **1a–f** to 1,2-naphthoquinones **2a–f**. Yields and selectivities were comparable to those obtained employing traditional oil-bath heating.

Table 1
Optimisation of conversion of **1a–2a**

Entry	Temp. (°C)	Hold time[a]	Equivalents of SeO_2	Conversion[b]
1	70	15 min	2	20
2	70	1 h	2	65[c]
3	120	5 min	2	82
4	150	5 min	2	100
5	150	1 min	2	100
6	150	1 s	2	100
7	150	1 s	1	0
8	150	1 s	1.5	68

[a] Hold time is the time the microwave reactor holds the set temperature. In all cases, the reaction reaches the set temperature in less than 5 min and is allowed to cool over 20 min by standing at room temperature.
[b] Determined by ^{1}H NMR spectroscopy.
[c] Extensive decomposition observed.

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Table 2
Oxidations of substituted 1-tetralones

Entry	Tetralone	R^1	R^2	R^3	R^4	Product	Isolated Yield (%)
1	**1a**	H	H	H	H	**2a**	44[a]
2	**1b**	H	H	OMe	H	**2b**	64
3	**1c**	H	OMe	H	H	**2c**	56
4	**1d**	H	H	OMe	OMe	**2d**	38[a]
5	**1e**	Me	H	H	H	**2e**	71
6	**1f**	H	Me	H	Me	**2f**	60

[a] Extensive decomposition occurred during chromatographic purification on silica gel.

All reactions were run on a CEM Discover laboratory microwave reactor. 4-Methyl-1-tetralone was synthesised, according to the literature procedure.[9] All previously reported compounds matched literature spectral data and full characterisation of new compounds follows.[5,10]

General procedure: 5,7-Dimethyl-1,2-naphthoquinone (**2f**). To an oven dried microwave vessel equipped with a magnetic stirrer was added 5,7-dimethyl-1-tetralone (174 mg, 1 mmol), finely ground selenium dioxide (220 mg, 2 mmol) and glacial acetic acid (1 mL). The vessel was then sealed and irradiated with microwave heating to 150 °C with a maximum of 300 W holding for 1 s. The vessel was allowed to cool to RT prior to dilution with 3 mL CH_2Cl_2 and filtering through Celite (4.25×10 cm plug) eluting with CH_2Cl_2. The volatile solvents were removed in vacuo before purification by flash chromatography (40% ethyl acetate/hexanes with 1% acetic acid and N_2 as pressurising gas) to yield the *title compound* (112 mg, 60%) as a red-brown solid. Mp 119–122 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.77 (br s, 1H, ArH), 7.70 (d, J = 10 Hz, 1H, H4), 7.26 (br s, ArH, 1H), 6.35 (d, J = 10 Hz, 1H, H3), 2.44 (s, 3H, CH_3), 2.36 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 181.2, 179.9, 142.0, 141.5, 138.6, 137.8, 132.3, 130.2, 129.5, 126.2, 21.3, 18.8. IR ($CDCl_3$) ν 2958, 2928, 2872, 1678, 1663, 1469, 1261 cm^{-1}. ESI-MS $(M+Na)^+$ = 209 *m/z*. Microanalysis Calcd ($C_{12}H_{10}O_2$) C, 77.40; H, 5.41. Found: C, 76.97; H, 5.26.

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