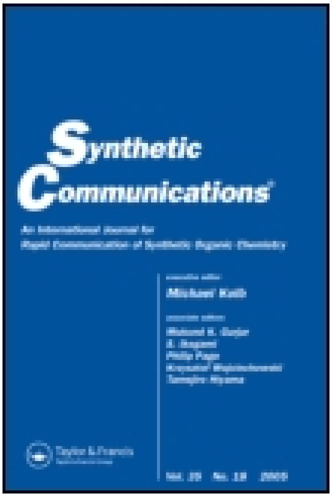

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Reaction of Hydroquinones with Supported Oxidizing Reagents in Solvent-Free Conditions

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To cite this article: J. Gómez-Lara , R. Gutiérrez-Pérez , G. Penieres-Carrillo , J. G. López-Cortés , A. Escudero-Salas & C. Alvarez-Toledano (2000) Reaction of Hydroquinones with Supported Oxidizing Reagents in Solvent-Free Conditions, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 30:15, 2713-2720

To link to this article: http://dx.doi.org/10.1080/00397910008086896

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SYNTHETIC COMMUNICATIONS, 30(15), 2713–2720 (2000)

REACTION OF HYDROQUINONES WITH SUPPORTED OXIDIZING REAGENTS IN SOLVENT-FREE CONDITIONS

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Abstract. Supported MnO_2 or HNO_3 on bentonitic clay cleanly oxidize some hydroquinones under infrared or microwave irradiation to the corresponding quinones with excellent conversion in short reaction times, using an easy and solvent-free approach.

The longstanding interest on quinones stems mainly from their structural diversity and also by their broad scope of applications such as polymerization inhibitors, intermediates for drugs, agrochemicals, dyes, etc.[1]. The simplest method -and by far the most common- for the conversion of hydroquinones to

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Dedicated to Dr. Jacobo Gómez Lara, recently deceased

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quinones is using a large array of oxidizing reagents. Thus, lead dioxide, chromium trioxide, bromine, Frémy's salt, hydrogen peroxide, etc., are among the most widely employed reagents[2]. Also, some recent patents concerning the oxidative step of hydroquinones to quinones have been reported using, *inter alia*, catalysts supporting copper salts[3], sulfuryl chloride[4], by peroxide and catalysts containing one or more transition elements[5], etc. Most of these methods present, however, several disadvantages, such as the use of harmful or deleterious reagents and expensive materials. On the other hand, it has been shown that bentonitic earth displays acid catalyst properties in a wide-spread series of oxidative solvent-free processes, e.g., using MnO_2/Bentonite or HNO_3/Bentonite systems, particularly under the influence of infrared or microwave irradiation[6-10].

We now wish to report our main results on a simple and straightforward method for the reaction of hydroquinones with MnO_2 or HNO_3 supported on a bentonitic earth[11], under infrared or microwave irradiation and in solvent-free conditions. Our results are summarized in Table 1.

As can be seen from the Table, 2-substituted hydroquinones give the corresponding quinones (**1-3**). For these reactions, the oxidizing reagent/energy source combination is critical for both reaction time and percent conversion to the desired product. The best conversion with the shortest reaction time was obtained in the HNO_3/Bentonite system under microwave irradiation. Furthermore, always is the microwave energy the best choice.

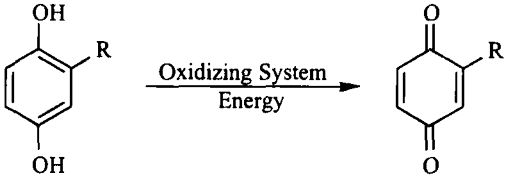
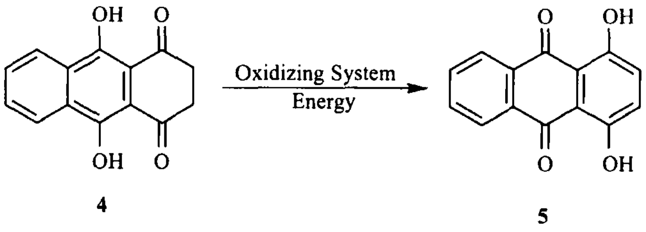


Table 1. Reaction of Hydroquinones

Product	R	Percent Conversion[a] (Reaction time, min)[b]				Reported M.p.[c] (Ref. 12)
		MnO$_2$/Bentonite		HNO$_3$/Bentonite		
		IR	Microwave	IR	Microwave	
1	OMe	0 (15)	100 (15)	92 (15)	100 (1)	145
2	Me	19 (15)	100 (5)	100 (15)	100 (3)	69
3	Cl	20 (15)	66 (15)	88 (15)	100 (10)	57
5		40(15)	71(15)	81(15)	100(10)	200-202
7		N.R.[d]	N.R.	30(15)	30(15)	--

[a] Determined by GC (see experimental part).
[b] Optimized reaction time.
[c] Experimental M.p. are the same than the reported values.
[d] No reaction was detected.

In the oxidation reaction of leucoquinizarin (**4**), the 1,4-dihydroxy-9,10-anthraquinone or quinizarin (**5**) was formed. Here, also the HNO$_3$/Bentonite system was the best oxidizing reagent using microwave irradiation.



4 **5**

Finally, in reference to the 1,8-dihydroxy-9,10-anthraquinone (**6**), a mononitration reaction is observed with the HNO_3/Bentonite system employing either infrared or microwave energy, while with the MnO_2/Bentonite system there is not reaction at all. Formation of (**7**) as the main product can be considered as unexpected and, to our knowledge, this compound has not been previously reported. No oxidized products were detected in this experiment.

It is worth to note that the anthracene derivatives are more reactive than their benzene analogs and give rise to polysubstituted products. The HNO_3/Bentonite system has previously been employed for the preparation of 7-nitroderivatives in the allylic nitration of 3β-sitosterol and cholesterol acetate.[6]

In summary, a clean and mild oxidation reaction of hydroquinones to the corresponding quinones -along with an unexpected nitration reaction- giving excellent conversion on very short reaction times, in an easy-to-use and solvent-free approach using supported oxidizing reagents is reported.

Experimental part.

Reaction with Microwave Energy. In a typical reaction, a mixture of 0.5 g of the hydroquinone and 3.0 g of the oxidizing reagent/Bentonite was irradiated using an open Pyrex flask, in a dry medium, with a domestic microwave oven (Kenmore Model DMR-604, 2450 MHz) to the maximun power (all experiments are done on the same scale). The mixture was irradiated to reach the highest percent of conversion in the shortest reaction time. After cooling down to room temperature, the reaction mixture was poured into a Büchner filter containing celite and washed with dichloromethane. Conversion was determined by the GC technique (Hewlett Packard Model 5890/1 FID with H_2 as carrier gas, crosslinked 5% PhMe silicone column 25m X 0.32mm).

Reaction with Infrared Energy. The mixture prepared as above was magnetically stirred in a round-bottomed flask equipped with a reflux condenser and irradiated with an infrared apparatus as reported by Pool and Teuben[13], using a commercial lamp (Osram, 250 watts). The reaction mixture was treated and analyzed as for the microwave energy system.

All products, after purification by chromatography, were characterized by their physical constants and spectroscopic data.

1,8-Dihydroxy-4-nitro-9,10-anthraquinone (**6**). M.p.=232-234°C. I.R. (cm^{-1}), KBr: 1675 and 1625 (C=O); 1544 and 1371 (NO_2). MS-EI (m/z): 285 (M^+, BP).

HR-MS: Found 285.0270 ($C_{14}H_7NO_6$); Calc. 285.0273. ^{1}H NMR (300 MHz, Benzene-d_6, δ ppm): 12.04 (s, 1H, O-$\underline{H}_1$); 11.49 (s, 1H, O-$\underline{H}_8$), both signals disappear with D_2O; 7.37 (dd, 1H, C-$\underline{H}_6$); 6.83 (m, 2H, C-$\underline{H}_5$ and C-$\underline{H}_7$); 6.56 and 6.47 (AB system, 2H, $\underline{H}_3$ and $\underline{H}_2$, respectively). ^{13}C NMR (75 MHz, Benzene-d_6, δ ppm): 191.72 ($\underline{C}_{10}$=O), 178.37 ($\underline{C}_9$=O), 162.97 ($\underline{C}_1$OH), 162.41 ($\underline{C}_8$OH), 147.56 ($\underline{C}_4NO_2$), 137.65 ($\underline{C}_5$H), 130.67 ($\underline{C}_{14}$), 128.30 ($\underline{C}_{11}$), 128.00 ($\underline{C}_{13}$), 127.66 ($\underline{C}_{12}$), 124.30 ($\underline{C}_3$H), 124.00 ($\underline{C}_6$), 120.83 ($\underline{C}_2$), 120.09 ($\underline{C}_7$).

Acknowledgment. We thank DGAPA-UNAM IN202597 for the financial support.

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11. Clay used is Tonsil Actisil FF (commercial name). Chemical composition: On examination by X-ray fluorescence, the clay employed in this study was found to have the following composition (in %): SiO_2, 63.5, Al_2O_3, 12.7; MgO, 3.1; Fe_2O_3, 4.9; CaO, 1.5; K_2O, 3.1; TiO_2, 0.6; MnO, 0.03; Na_2O, 0.8; P_2O_5, 0.1; H_2O (110°) 9.5. The commercial acid-activated material was obtained from Tonsil Mexicana and analyzed with a Phillips spectrometer using Cr primary radiation. The measured specific surface area was 161.074 m^2/g (B.E.T. N_2), and the pore volume was 0.3235 cm^3/g. The acidity by NH_3 thermodesorption was 12.107 μmol/mg. The particle size was 325 mesh. Comercial price to date: $ 0.35 US/Kg.
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Received in the USA 11/3/99