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SHORT COMMUNICATIONS

Efficient Solvent-Free Oxidation of Phenols to *p*-Quinones with Iodic Acid on the Surface of K10 Montmorillonite*

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Solid-phase organic reactions make it possible to obtain various compounds and constitute an attractive field of organic synthesis [1–3]. The use of montmorillonite clays ensured exceptionally important advances in manufacture of products of fine organic synthesis [1, 4]. Derivatives of quinones exhibit biological activity and are important intermediate products in the synthesis of drugs such as anthracycline antibiotics and anthracyclinones [5]. In addition, they are used as oxidants and aromatizers. Therefore, oxidation of phenols to the corresponding quinones is of great significance for organic synthesis. Although numerous procedures have been reported [6], search for new methods of oxidation of phenols to quinones remains an important problem. Reactions occurring in the absence of a solvent under microwave irradiation may be carried out in open vessels on a preparative scale [7].

The transformation of phenols into quinones may be effected with the aid of such oxidants as potassium bichromate [8], sodium nitrate [9], hydrogen peroxide [10], ozone [1], and some bacteria [12, 13]. Most these procedures require severe conditions [8, 10, 11], give poor yields of the target products [9, 10], and include laborious workup [12, 13].

In continuation of our studies on the use of microwave irradiation to accelerate chemical reactions [14], the present communication describes oxidation of phenols to the corresponding *p*-quinones with iodic acid (HIO_3) in the presence of K10 montmorillonite under microwave irradiation (see table). The polar character of phenol derivatives and iodic acid should favor their reaction in a microwave oven.

Both substituted phenols and unsubstituted compound were quickly oxidized to the corresponding quinones in the absence of a solvent. Various mineral supports were tested, in particular clay, aluminum oxide, K10 montmorillonite, and silica gel. The best results from the viewpoint of the purity of products were obtained with the use of K10 montmorillonite. The reactions were carried out by mixing the corresponding phenol with iodic acid in the presence of K10 montmorillonite, followed by irradiation of the mixture in a microwave oven or by heating on a water bath over a period indicated in table. No *o*-quinones were detected among the oxidation products. When potassium or sodium iodate was used as oxidant, the yields were lower. Poor yields were also obtained in the absence of K10 montmorillonite.

The mechanism of oxidation was not studied specially. Presumably, the presence of montmorillonite as acidic support under conditions of microwave irradiation enhances the reactivity of phenols and favors formation of polar intermediates, thus increasing the reaction rate [15]. No oxidation occurred without microwave irradiation.

The use of iodic acid for oxidation of phenols to *p*-quinones was reported in [16, 17]. The reactions were performed in sulfuric acid as solvent. However, low yields of the products, high temperature, long reaction time, and laborious isolation procedure make this method unsuitable from the preparative viewpoint.

All reagents used were commercial products (Merck, Fluka, Aldrich). The products were isolated and purified by column chromatography. All the products were reported previously; they were identified by the melting points and IR and ^{1}H NMR spectra.

General procedure for oxidation of phenols to *p*-quinones. A mixture of iodic acid (2 mmol), K10 montmorillonite (2 g, specific surface 200 m^2/g, Fluka), and the corresponding phenol (1 mmol) was thoroughly ground in a mortar. The resulting mixture was irradiated in a microwave oven or heated on a boiling water bath under atmospheric pressure over

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Oxidation of phenols with iodic acid over K10 montmorillonite under microwave irradiation and on heating on a water bath

Substrate	Product	Microwave irradiation		Heating	
		reaction time, s (power, W)	yield,[a] %	reaction time, min	yield,[a] %
Phenol	1,4-Benzoquinone	40 (1000)	94	17	96
4-Hydroxyphenol	1,4-Benzoquinone	35 (750)	98	12	91
4-Bromophenol	1,4-Benzoquinone	35 (1000)	81	20	83
4-Chlorophenol	1,4-Benzoquinone	40 (1000)	85		
3-Methylphenol	2-Methyl-1,4-benzoquinone	30 (1000)	77	18	70
4-Aminophenol	1,4-Benzoquinone	30 (1000)	93	13	90
4-Dimethylaminophenol	1,4-Benzoquinone	40 (1000)	89	15	91
3-Chlorophenol	2-Chloro-1,4-benzoquinone	45 (1000)	90	25	81
1-Naphthol	1,4-Naphthoquinone	50 (750)	93	20	97
1,4- Dihydroxynaphthalene	1,4-Naphthoquinone	30 (500)	98	10	98
1,8-Dihydroxynaphthalene	8-Hydroxy-1,4-naphthoquinone	50 (1000)	91	22	92

[a] Yield of the isolated product.

a period indicated in table. The progress of the reaction was monitored by thin-layer chromatography using ethanol–hexane (1:4) as eluent. When the reaction was complete, the mixture was treated with methanol, the extract was evaporated to dryness, the residue was dissolved in chloroform, the solution was washed with 5% aqueous solution of sodium hydroxide to remove unreacted phenol, the solvent was distilled off, and the residue was purified by column chromatography.

To conclude, it should be emphasized that the proposed solvent-free procedure for oxidation of phenols to the corresponding *p*-quinones with iodic acid on the surface of K10 montmorillonite under microwave irradiation is advantageous due to its simplicity and high selectivity; moreover, it overcomes the main drawback of iodic acid as oxidant, namely its poor solubility in organic solvents.

REFERENCES

1. Balogh, M. and Laszlo, P., *Organic Chemistry Using Clays*, Berlin: Springer, 1993, p. 108.
2. Laszlo, P., *Preparative Chemistry Using Supported Reagents*, San Diego: Academic, 1987, p. 29.
3. Clark, J.H., Cullen, S.R., Barlow, S.J., and Bastock, T.W., *J. Chem. Soc., Perkin Trans. 2*, 1994, p. 2013.
4. Sieskind, O. and Alberch, P., *Tetrahedron Lett.*, 1993, vol. 34, p. 1197.
5. Aromon, F., Franceschi, G., and Penco, A., *Tetrahedron Lett.*, 1967, p. 1007.
6. Hansen, D.W.J., Pappo, R., and Garland, R.B., *J. Org. Chem.*, 1988, vol. 53, p. 4244.
7. Marko, I.E., Giles, P.R., Tsukazaki, M.S., Brown, M., and Urch, C.J., *Science*, 1996, vol. 247, p. 2044.
8. Rao, A.V., Chavan, S.P., and Sivadasan, L., *Tetrahedron*, 1986, vol. 42, p. 5065.
9. Martin, E.I. and Fieser, L.F., *Org. Synth.*, 1995, collect. vol. 3, p. 633.
10. Kar, B.C., *J. Indian Chem. Soc.*, 1937, vol. 14, p. 291.
11. Kashtanov, L.L. and Oloshchuk, O.N., *Zh. Obshch. Khim.*, 1937, vol. 7, p. 1413.
12. Folpmers, T., *Leeumenhoek*, 1937, vol. 1, p. 169.
13. Ges, B., *Physiol. Exp. Pharmacol.*, 1937, vol. 85, p. 173.
14. Varma, R.S. and Dahija, R., *Tetrahedron Lett.*, 1997, vol. 38, p. 8819.
15. Perreux, L. and Loupy, A., *Tetrahedron Lett.*, 2001, vol. 57, p. 9199.
16. Evans, W. and Dehn, W.M., *J. Am. Chem. Soc.*, 1930, vol. 52, p. 3647.
17. Williams, R.J. and Woods, M.A., *J. Am. Chem. Soc.*, 1937, vol. 59, p. 1408.