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Oxidation of Aromatic Amines to Quinones by Iodic Acid under Microwave Irradiation in the Presence of Montmorillonite K10 and Silica Gel

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Summary. A variety of aromatic amines are oxidized to their corresponding quinones in excellent yields by supported iodic acid under microwave irradiation and solvent free conditions.

Keywords. Aromatic amines; Iodic acid; Quinones; Solvent free oxidation; Microwave (MW) irradiation.

Introduction

Quinone derivatives are important bioactive materials and important intermediates in the preparation of medicines, *e.g.* anthrocycline antibiotics and anthrocyclinones [1]. Therefore, the oxidation of aromatic amines to quinones using simple methods can be very valuable. Solid phase reactions can be useful because of their high efficiency, environmental safety, and simple work up procedures [2–4].

Recently, microwave induced rate acceleration technology has become a powerful tool for synthetic purposes because of the enhanced selectivity, easy reaction conditions, rapid reactions, and increased yields [5]. The oxidation of aromatic amines to quinones is an important reaction in organic chemistry and a variety of oxidizing reagents such as potassium dichromate [6], ferric chloride [7], sodium nitrate [8], silver and lead oxide [9], hydrogen peroxide [10], potassium nitrosodisulfonate [11], lead tetraacetate [12], and hypochlorite ion [13] have been used.

Most of the reported reagents have strong oxidative power [6, 10, 11], give low chemical yields [8, 9], and some require tedious work up.

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Here we report the use of iodic acid on montmorillonite K10 and also silica gel as an oxidant for converting aromatic amines to the corresponding *para*-quinones under MW radiation. Polarity of amine derivatives and iodic acid makes them good candidates for reactions in a microwave oven.

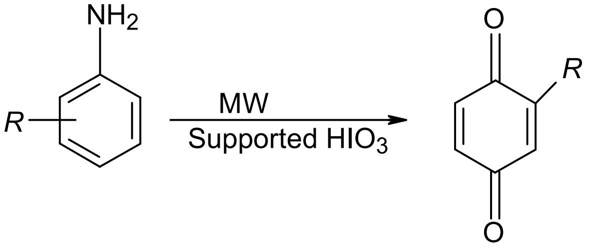
Although we have not experimentally established the mechanism of formation of the products, it seems that existence of silica gel and montmorillonite as an acidic support under microwave irradiation can accelerate this new oxidation by increasing the reactivity of the amine derivatives and also by supporting the formation of polar intermediates [14].

Results and Discussion

Supported HIO_3 on montmorillonite K10 is an excellent oxidant for aromatic amines to quinones as shown in Scheme 1. *Ortho*-quinones are not produced by this reagent except in the case of ortho amino- and hydroxyanilines. Aliphatic amines are converted to various products.

Table 1 lists a variety of aromatic amines oxidized with supported HIO_3 to the corresponding quinones. All yields refer to isolated products.

The following experiments have been performed to check the efficiency of our method. When this reaction was done on a water bath yields were much lower than



Scheme 1

Table 1. Oxidation of aromatic amines with supported HIO_3 under microwave irradiation

Entry	Substrate	Time/s/ Power/w	Temperature/ °C	Product	Yield/% a	Yield/% b
1	aniline	30/750	60	1,4-benzoquinone	63	51
2	4-hydroxyaniline	20/750	68	1,4-benzoquinone	85	37
3	2-hydroxyaniline	20/1000	67	1,2-benzoquinone	76	60
4	2-aminoaniline		65	1,2-benzoquinone	68	59
5	4-aminoaniline	20/1000	65	1,4-benzoquinone	61	43
6	3-bromoaniline	30/1000	65	2-bromo-1,4-benzoquinone	53	28
7	N,N-dimethylaniline	60/1000	67	1,4-benzoquinone	48	45
8	4-hydroxynaphtylamine	20/750	61	1,4-naphtoquinone	88	49
9	1-aminonaphtalene	20/750	58	1,4-naphtoquinone	72	48

a. Results from montmorillonite K10; b. Results from silica gel

Table 2. Oxidation of aromatic amines with silica gel supported HIO_3 on a water bath

Entry	Substrate	Time/h	Product	Yield/%[a]
1	aniline	2	1,4-benzoquinone	31
2	4-hydroxyaniline	1	1,4-benzoquinone	35
3	2-aminoaniline	1	1,2-benzoquinon	23
4	4-aminoaniline	2	1,4-benzoquinone	28
5	3-bromoaniline	3	2-bromo-1,4-benzoquinone	18

[a] All yields refer to isolated products

under MW conditions (Table 2). In the absence of supporting surface, HIO_3 alone does not oxidize aromatic amines. When the reaction was done using alumina as support yields were not acceptable.

Experimental

Chemicals were purchased from Merck, Fluka, and Aldrich chemical companies. Products were separated and purified by column chromatography technique. All products are known compounds and were identified by their mp, IR and ^{1}H NMR spectroscopic properties.

General Procedure

Iodic acid (3 mmol), montmorillonite K10 (2 g, surface 200 m^2/g, Fluka), and aromatic amine (1 mmol) were crushed together using a mortal and pistol. The mixture was exposed to microwave irradiation or the vapor of boiling water (80°C) under normal atmospheric conditions for the indicated time (Table 1). The progress of the reaction was followed by TLC, using ethanol:*n*-hexane = 1:4 as eluent until the starting material was no longer visible. The mixture was extracted with methanol, the solvent was evaporated, and the products were purified by column chromatography over silica gel and identified by their mp, IR, and ^{1}H NMR spectroscopic properties.

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