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Iodobenzene Diacetate on Alumina: Rapid Oxidation of Alcohols to Carbonyl Compounds in Solventless System Using Microwaves†

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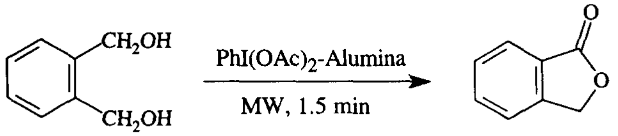
Abstract: In an environmentally benign solventless system, alcohols are rapidly oxidized to carbonyl compounds using alumina-supported iodobenzene diacetate (IBD) as an oxidant under microwave irradiation. © 1997 Elsevier Science Ltd.

The oxidation of alcoholic group to a carbonyl functionality is an important reaction in organic synthesis and several methods are available to accomplish this conversion under a variety of reaction conditions. Because of its important role in synthetic chemistry, this reaction continues to receive attention from the chemists in search for newer and selective methods of oxidation.[1]

The organohypervalent iodine reagents are commonly used oxidants in organic synthesis.[2] Iodoxybenzene,[3] *o*-iodoxybenzoic acid (IBX),[4] bis(trifluoroacetoxy)iodobenzene (BTI)[5] and Dess-Martin periodinane[6] have been used for the oxidation of alcohols and phenols in solution phase chemistry, but the use of iodobenzene diacetate (IBD) in this area, in spite of its low cost, has not been explored except for few examples of phenolic compounds.[7] Also, IBX has been reported to be explosive under heavy impact and heating over 200 °C.[8]

In recent years, the organic reactions on solid supports[9,10] and assisted by microwaves,[10-12] in particular, have gained special attention because of their enhanced selectivity, milder reaction conditions and associated ease of manipulation. In continuation of our ongoing program to develop environmentally benign reactions under solvent-free conditions using microwaves (MW), we explored the oxidation of neat alcohols with an equimolar amount of IBD that results in rapid formation of a syrupy thick liquid upon exposure to microwaves with rapid consumption of the starting alcohols. The analysis of the product obtained after work up revealed the formation of carbonyl compounds as summarized in Table. However, in the case of anisoin, the reaction resulted in the formation of mixture of products (Table, entry 7). In view of our earlier success with MW reactions on solid mineral supports,[10] which normally affords cleaner products, we repeated the reaction of anisoin with alumina-supported IBD. The reaction proceeded smoothly providing 96% yield of the corresponding carbonyl compound as shown in the table. The alumina-supported IBD appears to be a better choice since the reactions of neat alcohols with IBD in the absence of this mineral support are relatively slow and result in lower yields when compared to the alumina-supported reagent which provides higher yields and cleaner products in all cases (Table). The recyclability of the alumina support and the possible recovery of the generated iodobenzene are some of the environmentally benign attributes of this rapid protocol.

The procedure in all its entirety involves mixing of the neat alcohols with 1.1 equivalents of IBD doped on neutral alumina and irradiation of the reaction mixture in a microwave oven for the specified time (1-3 min) under solventless conditions. This rapid procedure avoids the over oxidation of alcohols to carboxylic acids. This process also eliminates the excessive use of corrosive solvents such as acetic acid and trifluoroacetic acid, and high boiling DMSO normally employed in reactions with relatively expensive hypervalent iodine reagents such as IBX and BTI.[3,4,6a] Interestingly, the reaction of 1,2-benzenedimethanol (Table, Entry 4) with 1.1 equivalents of the reagent remains incomplete. However, on oxidation with 2.2 equivalents of IBD doped on the same amount of alumina, the ensuing product undergoes intramolecular cyclization to give 1(3H)-isobenzofuranone[13] (Eqn.) and not the phthalic dicarboxaldehyde.



(Eqn.)

Hydroquinone and catechol are similarly oxidized to 1,4-benzoquinone and 1,2-benzoquinone in 69 and 46 % yields, respectively. The poor yields are presumably due to the adsorption of these quinones on alumina surface which could not be efficiently recovered.

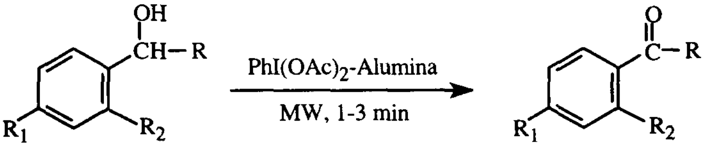


Table: Oxidation of alcohols using alumina-supported iodobenzene diacetate

Entry	R	R_1	R_2	$PhI(OAc)_2$		Al_2O_3-$PhI(OAc)_2$[b]	
				Time (min)	Yields (%)[a]	Time (min)	Yields (%)[a]
1.	H	H	H	2.0	89	1.0	94
2.	H	p-CH_3	H	2.0	88	1.0	92
3.	H	p-OCH_3	H	1.5	91	2.0	95
4.	H	H	CH_2OH	1.5	81	1.5	86
5.	CH_3CH_2	H	H	2.0	83	2.0	89
6.	C_6H_5CO	H	H	2.0	90	2.0	90
7.	p-$H_3COC_6H_4CO$	p-OCH_3	H	c	c	3.0	96
8	Hydroquinone			c	c	1.0	69
9	Catechol			c	c	0.5	43

[a] Unoptimized yields of the products exhibited physical and spectral characteristics in accord with the assigned structures. [b] IBD (0.355 g, 1.1 mmol) per gram of neutral alumina is ground using a pestle and mortar; the recovered alumina after removal of the products is reused without any loss of activity. [c] Mixture of products were formed.

General procedure: The oxidation of benzyl alcohol to benzaldehyde is representative of the general procedure employed. Benzyl alcohol (0.108 g, 1 mmol) and IBD (0.355 g, 1.1 mmol) doped on neutral alumina (1 g) are mixed thoroughly on a vortex mixer. The reaction mixture is placed in an alumina bath inside an unmodified household microwave oven and irradiated for a period of 1 min. On completion of the reaction, followed by TLC examination (hexane:AcOEt, 9:1, v/v), the product is extracted into dichloromethane and is neutralized with aqueous sodium bicarbonate solution. The dichloromethane layer is separated, dried over magnesium sulfate, filtered, and the crude product thus obtained is purified by column chromatography to afford pure benzaldehyde in 94 % yield. Alternatively, the crude products are charged on a silica gel column that provides iodobenzene on elution with hexane followed by pure carbonyl compounds in solvent system (hexane:ethyl acetate, 9:1, v/v).

That the effect is not purely *thermal*[14] is supported by the fact that this reaction could be completed in 2 hours in an oil bath at a comparable temperature of 80 °C. The limitation with aliphatic alcohols, however, still persists and the method gives a mixture of compounds.

In conclusion, the microwave-enhanced oxyhyperiodination reactions of alcohols are convenient, selective and environmentally benign protocols when compared to the conventional solution phase or heterogeneous oxidation reactions. The oxidative use of supported iodobenzene diacetate reagent under solvent-free conditions would generate newer applications of this and related hypervalent iodine agents in organic synthesis.

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