J. Chem. Research (S), 1997, 342–343†

Selective Oxidation of Arenes in Dry Media under Focused Microwaves†

Abdelouahad Oussaid and André Loupy*

*Laboratoire des Réactions Sélectives sur Supports, CNRS UA 478, ICMO, Université Paris XI,
Bâtiment 410, 91405 Orsay Cédex, France*

Arenes are oxidized into ketones within 10–30 min using $KMnO_4$ impregnated on alumina under microwave activation in dry media, instead of several days under classical conditions.

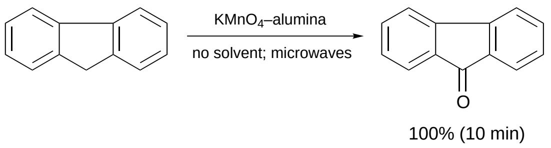
The use of solid supports in synthetic chemistry is a well established and environmentally friendly technology.[1–3] The oxidation of organic compounds with potassium permanganate adsorbed on solid supports (alumina, bentonite, silica gel) has especially been proved to be of noticeable efficiency.[3–7] The most significant advantages lie in increases in reactivity and selectivity when compared to homogeneous conditions. For instance, primary alcohols are oxidized into aldehydes without subsequent oxidation to carboxylic acid.[3,6]

It was recently shown that $KMnO_4$ adsorbed onto alumina could lead to selective oxidations of arenes at the benzylic position.[7] However, although the selectivity of this reagent is noteworthy, the reactions suffer from very long reaction times (up to 328 h) when performed at room temperature in the presence of 1,2-dichloroethane (DCE) as solvent. The same reaction has also been carried out using aqueous $KMnO_4$ in the presence of ultrasound.[8]

In this paper, we report a procedure where the oxidation was performed in dry media in order to improve the conditions and to prevent problems connected with solvent use (cost, handling, safety, pollution, decrease in reactivity by dilution of the reactants). Microwave activation rather than conventional heating was preferred, as solid supports are rather poor thermal conductors (with consequently an important gradient in temperature inside the materials), whereas they behave as strong microwave absorbents (and therefore with a better homogeneity in temperature,[9,10]). Consequently, reactions were generally faster and the obtained products more pure.[10,11] In this context we should point out that the permanganate oxidation of toluene to benzoic acid in basic solution gives only a poor yield (40%) and is reported to result in a violent explosion due to high pressures developed.[12] Oxidations of dihydropyridines, esters and alcohols have been subsequently described in ‘dry media’ using MnO_2 on bentonite under microwave irradiation.[13,14]

For these reasons, we considered the behaviour of $KMnO_4$ on alumina in ‘dry media’ in a monomode reactor (Synthewave 402, Prolabo) in order to take advantage of focused microwaves and to have a continuous temperature control followed by IR detection.[15] The main results are indicated in Table 1.

The oxidations gave excellent yields within very short reaction times. For instance, the reaction time was reduced from 118 h to 10 min for oxidation of fluorene into fluorenone (Scheme 1) and from 282 h to 30 min for diphenylmethane oxidation into benzophenone.



Scheme 1

In summary, our method describes a noticeable improvement in reaction conditions for the selective oxidation of arenes and takes advantage of both dry media technology and microwave activation (under the same conditions of time and temperature, yields were reduced to 40–70% by conventional heating). We have also shown that, in the case of 9,10-dihydroanthracene oxidation, anthracene is an intermediate product on the way to anthraquinone formation. Unfortunately, at the present time, the efficiency of this system is limited to diaryl compounds as its extension to indan, phthalan or toluene is problematic and will need further investigation.

Experimental

Preparation of Oxidative System.—Finely ground potassium permanganate (50 g) dissolved in water (100 ml) was added to alumina (acidic or neutral, Merck activity I, 63–200 nm; 200 g). After shaking for 15 min, the majority of the water was removed by evaporation under reduced pressure and the obtained powder was dried under microwave irradiation for 5 min.

Fluoren-9-one.—In a Pyrex matrix adapted to a Synthewave 402 monomode reactor, fluorene (2 mmol, 0.332 g) was added to the $KMnO_4$–alumina mixture (6 mmol, 4.74 g). After 5 min of mechanical stirring, the mixture was irradiated (under stirring) at 150 W for 10 min. At the end of exposure to microwaves, the mixture was cooled to room temperature and eluted with diethyl ether (50 ml). After filtration and solvent removal, the crude product was identified by comparison (GC and NMR) with an authentic sample.

Table 1 Permanganate oxidations in dry media under monomode microwave activation (emitted power = 150 W)

		Experimental conditions			Lit. (DCE)[b]	
Reactant	Product	*t*/min	*T*/°C[a]	Yield (%)	*t*/h	Yield (%)
Fluorene	Fluoren-9-one	10	140	100	118	100
Xanthene	Xanthone	12	120	100	67	92
Anthrone	Anthraquinone	10	107	86	75	100
Diphenylmethane	Benzophenone	30	110	97	282	92
9,10-Dihydroanthracene	Anthracene (**1**) + Anthraquinone (**2**)	30	103	**1** (70) + **2** (9)	121	**2** (98)
	Anthracene (**1**) + Anthraquinone (**2**)	120	110	**1** (6) + **2** (84)	121	**2** (98)

[a]Final temperature measured by IR detection. [b]Ref. 7.

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*To receive any correspondence (*e-mail:* aloupy@icmo.u-psud.fr).

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Received, 23rd September 1996; Accepted, 16th June 1997
Paper F/7/04561A

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