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Selective oxidation of alkylarenes in dry media with potassium permanganate supported on montmorillonite K10

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Abstract—The solvent-free oxidation of alkylarenes with $KMnO_4$ supported on montmorillonite K10 is reported. The beneficial effects of microwave and ultrasound irradiation on the reactions is described.

1. Introduction

Adsorption onto solid supports is known to cause a change in the properties of many reagents.[1] One of the most striking examples of a change in chemical reactivity and selectivity that has been reported to date is with the well-known oxidant potassium permanganate.[2]

It was recently shown that alkylarenes are oxidized at the benzylic position when treated under heterogeneous conditions with $KMnO_4$ adsorbed on a solid support such as $CuSO_4{\cdot}5H_2O$,[3] Al_2O_3,[3,4] or zeolite.[5] Product yields were relatively good, but reaction times necessary for these yields were very long. For example 48–72 h when $CuSO_4{\cdot}5H_2O$ is the solid support and 66–328 h in the case of moist Al_2O_3 and 96 h in the case of zeolite.

In connection with our previous work on solid state oxidation,[6] we wish to report the results obtained from a study of the oxidation of alkylarenes with $KMnO_4$ adsorbed on the very inexpensive and readily available support, montmorillonite K10. The procedure gives products in good yields and avoids problems connected with solvent use (cost, handling, safety and pollution). Decreased reaction times are also realized because of increased reactivity of the oxidant in the solid state.

As can be seen from Table 1, alkylarenes are converted into the corresponding α-ketones in good yields under very mild conditions. The products are identical to those obtained under heterogeneous conditions where the reductant is dissolved in an inert solvent; however, the reaction times are reduced from a few days to a few hours at room temperature. As indicated in Scheme 1, the reaction is equally effective when oxygen is present in the side chain. Excellent yields of the corresponding lactones are realized when the side chain is an exocyclic ether.

Some alkylarenes such as indan, xanthene, fluorene and tetralin are very readily oxidized to the corresponding carbonyl compounds (entries 9–12), while the others such as *o*-xylene are completely resistant to oxidation (entry 7), possibly because of an unfavorable steric effect. The decreased reactivity of *p*-bromotoluene suggests that electron-withdrawing groups are deactivating. As similar observation has previously been made for the corresponding reactions carried out under heterogeneous conditions.[3] However, the results reported in Table 1 indicate that much shorter reaction times are required for the solvent free reactions, particularly if they are assisted by microwave or ultrasonic irradiation.

As can be seen from the results reported in Table 1, application of ultrasonic technology in these reactions decreases the time required to obtain good yields by a factor of about 10. Use of microwave irradiation decreases the required time by another order of magnitude. For example, the time required to convert fluorene into 9-fluorenone in 85–90% yield, 1440 min at room temperature in the absence of irradiation, is reduced to 120 min when ultrasonic irradiation is applied and to 10 min when microwave irradiation is used. As a consequence, it is possible to select the most

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Table 1. The oxidation of alkylarenes by potassium permanganate adsorbed on montmorillonite K10 under solvent free conditions. Effect of microwave and ultrasonic on yield and times required[a]

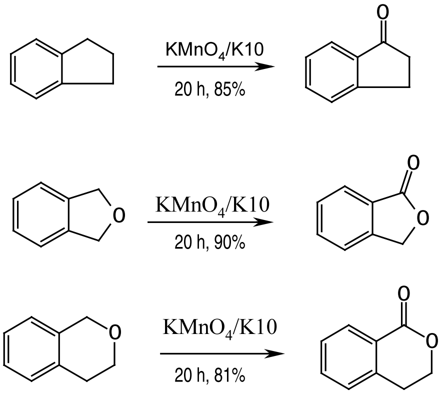
Entry	Alkylarene	Product	Yield/time[b]	Yield/time[c]	Yield/time[d]
1	Diphenylmethane	Benzophenone	86%/20 h	81%/2.5 h	78%/20 min
2	Ethylbenzene	Acetophenone	64%/19 h	52%/3.5 h	44%/12 min
3	Propylbenzene	Propiophenone	57%/20 h	54%/2.5 h	50%/20 min
4	Butylbenzene	1-Phenyl-1-butanone	60%/20 h	61%/3 h	63%/25 min
5	Toluene	Benzaldehyde	60%/18 h	52%/1.7 h	54%/12 min
6	*p*-Xylene	*p*-Methylbenzaldehyde	67%/20 h	53%/2.7 h	65%/35 min
7	*o*-Xylene	No reaction			
8	*p*-Bromotoluene	*p*-Bromobenzaldhyde	20%/20 h	12%/2 h	15%/30 min
9	Tetralin	α-Tetralone	87%/20 h	82%/2.5 h	82%/25 min
10	Indan	1-Indanone	85%/20 h	83%/2.5 h	78%/30 min
11	Xanthene	Xanthone	81%/22 h	86%/2 h	86%/10 min
12	Fluorene	9-Fluorenone	89%/24 h	87%/2 h	86%/10 min
13	Isochroman	Isochroman-1-one	81%/20 h	80%/2 h	80%/10 min
14	Phthalane	Phthalone	90%/20 h	86%/2 h	87%/15 min
15	2,3-Dihydrobenzofurane	No reaction			

[a] Isolated yields. Product identification is carried out by comparison of physical properties (melting points, mass spectra, infrared and NMR spectra) with literature values.

[b] Temperature = 23°C.

[c] Reaction subjected to ultrasonic irradiation.

[d] Reaction promoted by microwave irradiation.



Scheme 1.

appropriate conditions for a particular application. If time is of little importance, the reaction can be completed without expenditure of additional energy. However, if time is an important factor, energy can be applied in the form of either ultrasonic or microwave irradiation.

It was recently shown that $KMnO_4$ adsorbed onto alumina could lead to selective oxidation of alkylarenes at the benzylic position under MW irradiation.[7] However, the efficiency of that system was limited to diaryl compounds and extension of it to indan, phthalene and toluene was problematic. In this work, we were able to improve the previous method for oxidation of low boiling compounds by using a Teflon vessel. As indicated in Table 1, the oxidation of both diaryl and aryl alkyl compounds have been carried out in relatively high yields in a Teflon vessel irradiated by microwaves.

In summary due to its good reactivity and ease of product separation, $KMnO_4$ adsorbed on montmorillonite K10 can be recommended as a practical oxidant for benzylic oxidations in the solid state at room temperature.

2. Experimental

2.1. Oxidation of indan under classical condition

Potassium permanganate (3.16 g, 20 mmol) and montmorillonite K10 (6 g) were ground together in a mortar until a fine homogeneous powder was obtained.

Indan (0.24 g, 2 mmol) was added to this $KMnO_4$/K10 mixture (4.5 g, 9.9 mmol) in a 25 mL round bottomed flask and mixed magnetically at room temperature until TLC (eluent: hexane–ethyl acetate) analysis indicated a completed reaction (20 h). The residue was then washed with CH_2Cl_2 (2×20 mL). After filtration and removal of the solvent, the crude product was chromatographed on silica gel (eluent: hexane–ethyl acetate) to give purified product (0.22 g, 1.7 mmol, 85%) which was identified by comparison with authentic 1-indanone using TLC, melting point (39–41°C; lit.[8] 42°C), ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.63 (t, $^3J_{HH}$ 6.1 Hz, 2H), 3.09 (t, $^3J_{HH}$ 6.1 Hz, 2H), 7.08–7.80 (m, 4H) and MS: m/z (%) = 132 (M^+, 100), 104 (98), 78 (15), 51 (10).

2.2. Oxidation of isochroman in the presence of ultrasound irradiation

Isochroman (0.27 g, 2 mmol) and $KMnO_4$/K10 (4.5 g, 9.9 mmol) were finely mixed together and the reaction mixture irradiated in a 25 mL beaker. The progress of the reaction was monitored by TLC. When complete (150 min), the reaction mixture was washed with CH_2Cl_2 (2×20 mL). After filtration and solvent removal the crude product was chromatographed on silica gel (eluent: hexane–ethyl acetate) to give purified product (0.24 g, 1.6 mmol, 80%). Identification was by ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.10 (t, $^3J_{HH}$ 8.57 Hz, 2H), 4.56 (t, $^3J_{HH}$ 8.57 Hz, 2H), 7.20–8.20 (m, 4H) and MS: m/z (%) = 148 (M^+, 68), 118 (100), 90 (76), 63 (25), 39 (25).

2.3. Oxidation of tetralin under microwave irradiation

In a 25 mL Teflon beaker, tetralin (0.26 g, 2 mmol) was added to $KMnO_4$/K10 (4.5 g, 9.9 mmol). After 3 min of mechanical stirring, the mixture was irradiated at medium power for 25 min. At the end of exposure to microwave irradiation, the mixture was cooled to room temperature and eluted with CH_2Cl_2 (2×20 mL). After filtration and solvent removal the crude product was chromatographed on silica gel (eluent: hexane–ethyl acetate) to give purified product (0.24 g, 1.7 mmol, 82%). Identification was by ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.01–2.18 (m, 2H), 2.50–2.65 (m, 2H), 2.80–3.01 (m, 2H), 7.20–8.10 (m, 4H) and MS: m/z (%) = 145 (M^+–1, 15), 130 (100), 91 (58), 57 (25).

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References

1. (a) Smith, K., Ed. *Solid Supports and Catalysis in Organic Synthesis*; Ellis Harwood and PTR Prentice Hall: New York, 1992; (b) Laszlo, P. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 7, p. 839.
2. Lee, D. G. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, 1995; pp. 4274–4281.
3. Noureldin, N. A.; Zhao, D.; Lee, D. G. *J. Org. Chem.* **1998**, *62*, 8772.
4. Zhao, D.; Lee, D. G. *Synthesis* **1994**, 915.
5. Sreekumar, R.; Padmakumar, R. *Tetrahedron Lett.* **1997**, *38*, 5143.
6. Shaabani, A.; Lee, D. G. *Tetrahedron Lett.* **2001**, *42*, 5833.
7. Oussaid, A.; Loupy, A. *J. Chem. Res. (S)* **1997**, 342.
8. *CRC Handbook of Chemistry and Physics*, Weast, R. C., Ed.; The Chemical Rubber Co.: Boca Raton, 1975–1976; p. C342.