EFFECTS OF ULTRASOUND AND MICROWAVE IRRADIATION ON THE GREEN OXIDATION OF ALKYLARENES BY $KMnO_4/CuSO_4\ 5H_2O$

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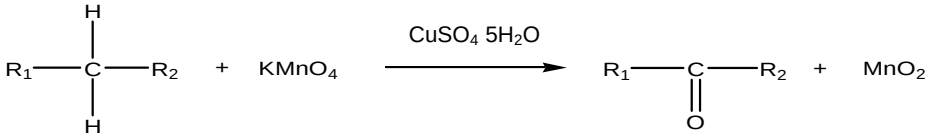
ABSTRACT: *Potassium permanganate oxidized some alkylarenes such as ethylbenzene (**1**), propylbenzene (**2**), diphenylmethane (**3**), cumene (**4**), 1-bromo-2-phenylethane (**5**), indane (**6**), tetraline (**7**), and fluorene (**8**) at the benzylic position to form the corresponding aromatic ketones under solventless reaction conditions. Under the assisstance of ultrasound and microwave irradiation, the reaction times were reduced remarkably without a decrease of the yield. Reaction factors including the molar ratio of substrates, $KMnO_4$, $CuSO_4\ 5H_2O$, reaction time, microwave power were optimized to achieve the highest conversion yields and product selectivities.*

Key words: *Alkylarene, oxidation, permanganate, copper sulfate pentahydrate, ultrasound, microwave.*

1.INTRODUCTION

Aromatic ketones are important intermediate products for the procurement of perfumes, drugs, and pharmaceuticals. In recent years, the preparation of aromatic ketones by the oxidation of alkyl groups close to an aromatic ring has been investigated in order to replace former method based on the Friedel-Crafts reaction. Erosive and toxic waste produced by the Friedel-Crafts acylation reaction is a main reason for improvement in synthetic ways to aromatic ketones.[1] The oxidation reactions were performed under heterogeneous conditions by $KMnO_4$ absorbed on $CuSO_4\ 5H_2O$,[2] Al_2O_3,[3] zeolite,[4] montmorilonite K10.[5] Recently, the solventless oxidations were performed by using dichromate ion absorbed on alumina,[6] or $KMnO_4$ mixed with $CuSO_4\ 5H_2O$.[7,8]

Solventless reaction is important in Green chemistry.[9-11] It prevents from problems of solvent such as charges, handling, safety and pollution. In general, the solventless reaction gives high yield in a short time, because the oxidant is spread widely on the surface of the solid support. Our intentions with this research are to pay attention to the reaction stoichiometry under solventless reaction conditions and under the irradiation of ultrasound and microwave in order to optimize the reaction conditions for each substrate, and to observe the influences of microwave and ultrasound irradiation. Besides, manganese dioxide and copper sulfate pentahydrate are easily collected and obtained with high yield.



1-8 **1a-8a**

Scheme 1. Oxidation of alkylarenes at benzylic position.

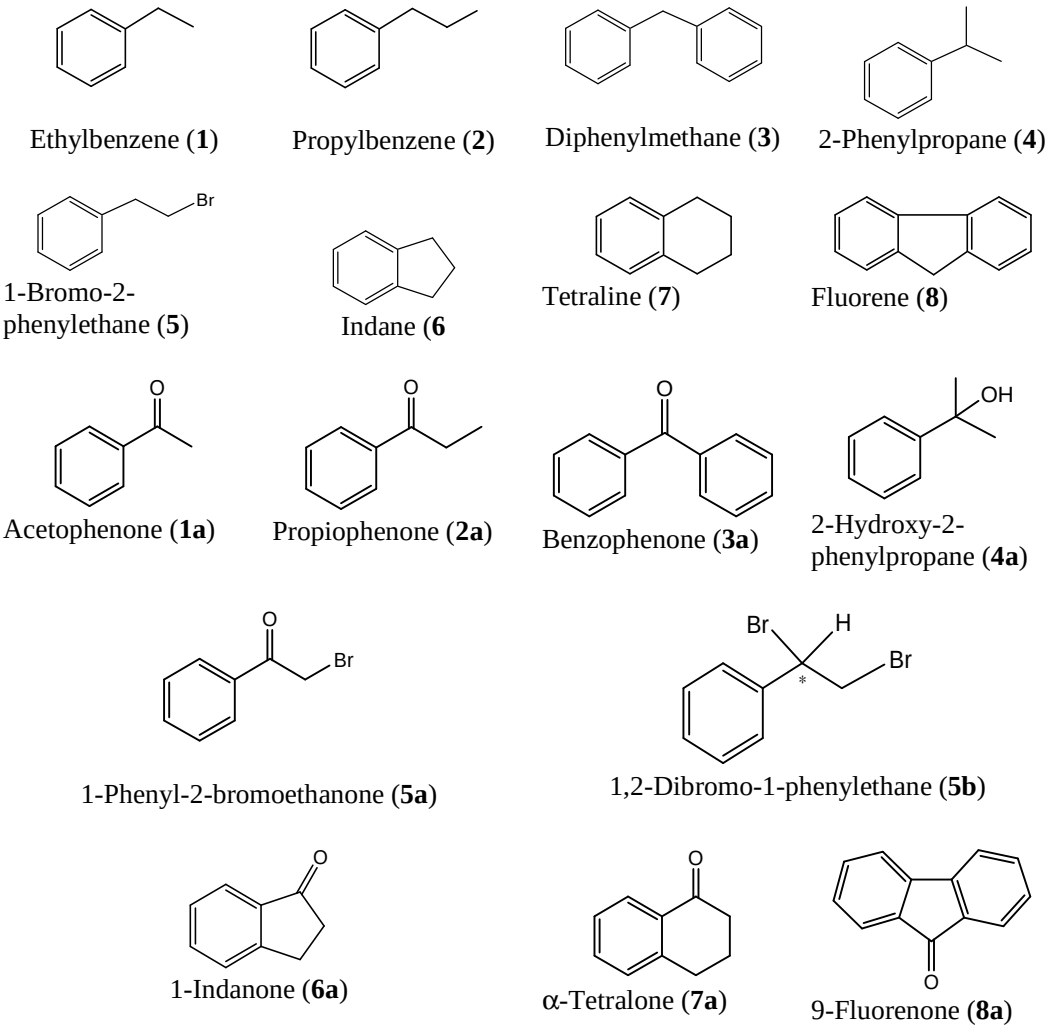


Fig. 1 Structure of substrates and products in the oxidation of alkylarenes.

2.RESULTS AND DISCUSSION

The stoichiometric factor investigated on the oxidation of diphenylmethane in two methods (microwave and ultrasound) (Fig. 2) gave evidence that the best molar ratio of substrate, $KMnO_4$, and $CuSO_4$ $5H_2O$ was 3:12:24. This ratio, observed again also for the oxidation of indane, confirmed that it was the best molar ratio for the oxidation of alkylarenes and arenes.

This oxidant, in the following referred to as **PP/2CSP** (**p**otassium **p**ermanganate absorbed on a **two-fold** molar amount of **c**opper **s**ulfate **p**entahydrate), was chosen as the standard oxidant in our subsequent experiments. It should be stressed that **PP/2CSP** must be prepared as described (Experimental).

Altogether 8 alkylarenes were subjected to oxidation by **PP/2CSP** under solvent-free reaction conditions, using four different methods. In method A, fair to excellent yields were

obtained under mild conditions (33-34 ^{o}C) during long reation times (20-48 hours). Under the assistance of ultrasound (Method B, Table 1), the reaction times were found shortened considerably (3.5-8 hours) although the yields of the products were only slightly improved. Microwave irradiation had no strong effect on this reaction type. The yields under conventional heating conditions were lower than under microwave irradiation conditions.

There were some exceptional cases: i) in the case of oxidation of **5**, the reaction temperature provided by microwave or conventional heating increased the yield of **5b**, ii) in case of the oxidation of **4**, the assistance of microwave or ultrasound increased the formation of **1a** by cleavage of a methyl group, and iii) **6a** and **7a** became over-oxidized to indan-1,3-dione and tetrahydronapthalene-1,4-dione.

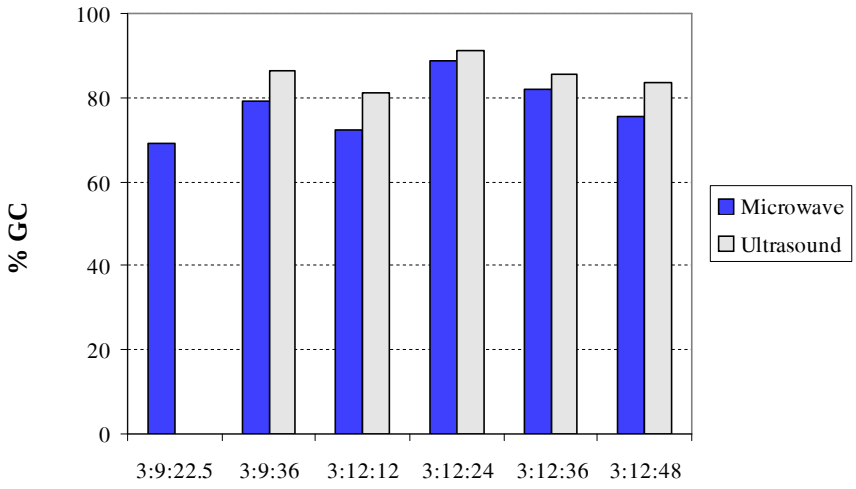


Fig. 2 Influences of the molar ratio diphenylmethane (**3**):$KMnO_4$:$CuSO_4$ $5H_2O$ on the efficiency of the oxidation of diphenylmethane under solvent-free conditions and under microwave irradiation at 240 W (for 6-8 min), or ultrasound irradiation (for 5 hours).

Table 1. Oxidation yield of alkylarenes following four different methods.[a]

Substrate	Product	Method A Y (%GC, t[b])	Method B Y (%GC, t[b])	Method C Y (%GC, t[b*], P[c])	Method D Y (%GC, t[b*], temp.[d])
1	**1a**	62 (75, 20)	97 (100, 3.5)	58 (70, 8.7, 250)	56 (66, 8.7, 94)
2	**2a**	-	32 (33, 7)	38 (42, 8.1, 630)	-
3	**3a**	87 (96, 28)	99 (100, 6)	82 (93, 7.7, 150)	83 (97, 7.7, 96)
4	**4a**	30 (35, 48)	36 (43, 5)	16 (26, 9.2, 350)	-

	1a	7 (7, 48)	24 (25, 5)	10 (15, 9.2, 350)	-
5	**5a**	67 (68, 48)	71 (75, 8)	30 (36, 4.8, 350)	24 (29, 4.8, 100)
	5b	5 (7, 48)	12 (18, 8)	13 (22, 4.8, 350)	13 (22, 4.8, 100)
6	**6a**	14 (17, 24)	78 (84, 5)	40 (44, 4.0, 250)	20 (32, 4.0, 99)
7	**7a**	-	65 (73, 3)	52 (60, 10.6, 250)	40 (49, 10.6, 101)
8	**8a**	-	45 (52, 8)	40 (45, 12.4, 250)	32 (40, 12.4, 100)

[a] Yield (Y) was calculated based on %GC. All results were optimized.
[b] t = hr, [b*] t = min. [c] P = Watt. [d] temp. = ^{o}C.

3.CONCLUSION

Comprehensive experimental work has demonstrated the oxidation ability of **PP/2CSP** to convert alkylarenes into aromatic ketones in high yields. Ultrasound assistance made the reaction times much shorter than found by the shaking method. Microwave irradiation enhanced the yields quickly in the shorter time, however the reaction has not performed completely. In reactions leading to product competition, microwave assistance lead to a decrease of the product selectivity.

4.EXPERIMENTAL

4.1.Instrumentation

For solvent-free reactions, ultrasound irradiation was performed by means of a BRANSON 1210E-MT ultrasonic bath, operating at frequency 47 kHz. Microwave irradiation was performed by means of a batch microwave oven CEM MDS 200. GC/MS analyses were performed on a Hewlett Packard 5890 GC 5971A MS apparatus equipped with a J&W DB-5MS capillary column (30 m, 0.25 mm i.d., 0.25 μm film thickness) and a Hewlett Packard 7673A autosampler. NMR spectra were recorded on a Varian Mercury 300 NMR spectrometer. Infrared spectra were recorded on a Perkin Elmer FT-IR 2000 spectrometer.

4.2.Chemicals

All chemicals used were from Aldrich or Merck. All liquid chemicals were distilled before use to secure maximum purity (~100%, checked by GC/MS).

4.3.Preparation of oxidants (including PP/2CSP)

Copper sulfate pentahydrate was dissolved completely in de-ionized water. Then $KMnO_4$ was added, followed by a sufficient volume of de-ionized water to obtain a homogeneous solution. The solution was stirred for 10 minutes at 80 ^{o}C. Subsequently, water was removed from the solution by rotational evaporation, until the weight of the remaining solid mass was equal to the sum of the weights of the original ingredients. The obtained solid mass was ground in a mortar into a fine homogeneous powder.

4.4.Oxidation of alkylarenes into corresponding ketones under solvent-free reaction conditions (Method A)

7.89 g (12.00 mmol) of finely ground oxidant **PP/2CSP** were added to a 10 mL round-bottom flask containing the alkylarene (3.00 mmol) and ten glass balls (d = 2 mm). The flask was fitted to a shaking machine to be shaken at speed 280 r.p.m. for a specific period of time (Table 1). Then the reaction mixture was extracted with 4 x 15 mL of diethyl ether. The combined extracts were filtered through a 1.5–2 cm layer of celite 545, and then dried (anhydrous Na_2SO_4). After removal of the solvent by rotational evaporation, the purity of crude product was analysed by GC/MS. The pure ketone was isolated from the crude product by flash column chromatography (7 g silica gel, Davisil, grade 710, 4-20 μm, 60 A, 99%) using as eluent a mixture of hexane:dichloromethane and identified by NMR spectroscopy, and IR spectroscopy.

4.5.Oxidation of alkylarenes into corresponding ketones under solvent-free reaction conditions assisted by ultrasound irradiation (Method B)

7.89 g (12.00 mmol) of finely ground **PP/2CSP** were added to test tube (h=16 cm, d=1.4 cm) containing the alkylarene (3.00 mmol). The test tube was placed into an ultrasound bath, where the mixture of reactants was exposed to ultrasound irradiation for a specified period of time (Table 1). Subsequently the reaction mixture was worked up as described in Method A.

4.6.Oxidation of alkylarenes into corresponding ketones under solvent-free reaction conditions assisted by microwave irradiation (Method C)

7.89 g (12.00 mmol) of finely ground **PP/2CSP** were added to a test tube (h=16 cm, d=1.4 cm) containing also the alkylarene (3.00 mmol). The test tube was placed into a beaker, equipped to adhere test tubes, in the CEM oven. For each of the alkylarene, an irradiation programme was applied to determine the most efficient reaction conditions (with respect to maximum yield of product, most convenient irradiation energy (W), and shortest reaction time (minutes)), see Table 1. For every experiment performed, the temperature of the reaction mixture was measured immediately after reaction stop. Subsequently the reaction mixture was worked up as described in Method A.

4.8.Oxidation of alkylarenes into corresponding ketones under solvent-free reaction conditions assisted by conventional heating (Method D)

A test tube (h = 16 cm, d = 1.4 cm) containing 7.89 g (12.00 mmol) of finely ground **PP/2CSP** and 3.00 mmol of the alkylarene was placed in an oil bath heated to the temperature measured by reaction stop of the parrallel reaction run under microwave irradiation. The test tube was kept in the oil bath for a period of time corresponding exactly to that found at optimum by Method C. After cooling, the reaction mixture was worked up as described in Method A.

HIỆU ỨNG SIÊU ÂM VÀ VI SÓNG TRONG SỰ OXID HÓA "XANH" ALKILAREN BẰNG $KMnO_4/CuSO_4\ 5H_2O$

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TÓM TẮT: *$KMnO_4$ tẩm trên $CuSO_4\ 5H_2O$ có thể oxid hóa nhóm thế alkil của một số aren như: etilbenzen(**1**), propilbenzen(**2**), diphenilmetan(**3**), cumen(**4**), 1-bromo-2-pheniletan(**5**), indan(**6**), tetralin(**7**) và fluoren(**8**) tại vị trí benzil để hình thành các ceton tương ứng trong môi trường khô. Dưới sự hỗ trợ của siêu âm và vi sóng có thể rút ngắn thời gian phản ứng nhưng vẫn thu được hiệu suất cao. Phản ứng đã được tối ưu hóa các yếu tố ảnh hưởng đến phản ứng như tỉ lệ mol chất nền, $KMnO_4$, $CuSO_4\ 5H_2O$, thời gian, công suất lò vi sóng nhằm đạt được độ chuyển hóa cao nhất.*

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