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# Ultrasound Assisted Heterogeneous Permanganate Oxidations

Mária Mečiarová, Štefan Toma\* and Andrea Heribanová

*Department of Organic Chemistry, Faculty of Natural Sciences, Comenius University, Mlynska dolina CH-2 SK-842 15 Bratislava, Slovak Republic*

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**Abstract**—The ultrasound effect on the heterogeneous permanganate oxidation of benzyl alcohol and alkylarenes to the corresponding carbonyl compounds is examined. Application of ultrasonic irradiation leads to shorter reaction times as well as lower reaction temperatures.  $\text{KMnO}_4$  supported by copper sulfate pentahydrate in  $\text{CH}_2\text{Cl}_2$  is possible to use for selective oxidation of benzyl alcohol to benzaldehyde. © 2000 Elsevier Science Ltd. All rights reserved.

## Introduction

Potassium permanganate is an oxidant widely used in organic syntheses.  $\text{KMnO}_4$  is soluble in water and in mixtures of water and miscible organic solvents such as acetone, acetic acid, acetonitrile and pyridine.  $\text{KMnO}_4$  can also be used as an oxidant in nonpolar organic solvents, but the aid of phase-transfer agents or adsorption onto a solid support such as hydrated copper (II) sulfate, alumina or silica is necessary.<sup>1</sup>

Inorganic salts adsorbed onto solid supports are in general very useful agents in organic synthesis. Alkylbenzenes are oxidized to the corresponding carbonyl compounds with sodium bromate on the surface of cerium dioxide.<sup>2</sup> Active manganese dioxide supported on alumina is a very good oxidant for the selective oxidation of alcohols to aldehydes or ketones and in the case of  $\alpha,\beta$ -unsaturated alcohols,  $\alpha,\beta$ -unsaturated carbonyl compounds arise.<sup>3</sup> Benzyl ethers are oxidized to benzoate esters by potassium permanganate in dichloromethane with phase-transfer catalysis by triethylbenzylammonium chloride in fair to excellent yields.<sup>4</sup> Allylic, benzylic and saturated secondary alcohols are efficiently oxidized to the corresponding aldehydes or ketones by a solid mixture of  $\text{K}_2\text{FeO}_4$ ,  $\text{Al}_2\text{O}_3$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .<sup>5</sup> Oxidations of alcohols to aldehydes or ketones, aromatic amines to their corresponding azo derivatives and coupling of thiophenol into diphenyl disulfide were efficiently performed by potassium ferrate (VI) in the presence of the

K 10 montmorillonite.<sup>6</sup> Chromium (VI) dioxide with periodic acid oxidizes alkylbenzenes in  $\alpha$ -position to the corresponding ketones, but toluene is oxidized to benzoic acid.<sup>7</sup> Alkylarenes are oxidized to ketones within 10–30 min using  $\text{KMnO}_4$  impregnated on alumina under microwave activation in dry media, instead of several days under classical conditions.<sup>8</sup>

An interesting paper dealing with heterogeneous permanganate oxidations was published recently.<sup>9</sup> Alkylbenzenes are oxidized at the benzylic position when treated under heterogeneous conditions with potassium permanganate adsorbed on a solid support such as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and moist  $\text{Al}_2\text{O}_3$ , respectively. Using the substrate:oxidant molar ratio 1.4:10, yields of the products reached 30–95% but the reaction time necessary for such good yields was 48–72 h in the case of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as a solid support and 66–328 h in the case of moist  $\text{Al}_2\text{O}_3$ .

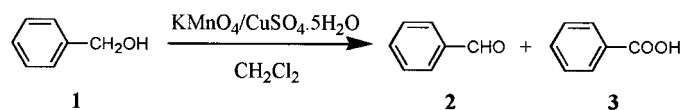
The advantages of the reactions on surfaces are as follows: easy separation of the product from the reagents or catalysts, new or better selectivities, faster reactions, lower reaction temperatures, safer, less toxic effluent can be used and other waste problems can be minimized. Problems encountered with these reactions, especially for large scale applications, include difficult heat and mass transport and difficult suspension stirring.<sup>10</sup> These difficulties and disadvantages can be eliminated by application of ultrasonic irradiation.

The main goals of this paper were:

1. to examine if it is possible to shorten the reaction time as well as to lower the reaction temperature by application of ultrasonic irradiation;

*Keywords:* ultrasound; heterogeneous oxidation; alkylarenes; alcohols; supported potassium permanganate.

\* Corresponding author. Tel.: +42-17-796208; fax: +42-17-796690; e-mail: toma@fns.uniba.sk



Scheme 1.

2. to find out experimental conditions for the selective oxidation of allyl and benzyl alcohols to aldehydes and to minimize overoxidation to carboxylic acids.

### Results and Discussion

To start our study we decided to examine carefully the oxidation of benzyl alcohol (Scheme 1). As follows from the Table 1, after 30 min of sonochemical reaction at the same substrate:oxidant ratio as in Ref. 9, the conversion of benzyl alcohol is 74% and more than 97% of the product is benzaldehyde. Just traces of benzoic acid were detected by  $^1\text{H}$  NMR analyses. After 1 h of sonochemical reaction the conversion slightly increased, but a larger amount of benzoic acid (12%) was detected in the crude product. The situation was similar after 1.5 h. Further extension of the reaction time increased the proportion of benzoic acid in the mixture of the products. After 3 h of sonochemical reaction conversion of starting material was 100% and the proportion of benzaldehyde to benzoic acid was approximately 1:1. Performing the same reaction without ultrasound for 0.5 h at room temperature gave just the starting material as was detected by  $^1\text{H}$  NMR of the reaction mixture. To achieve complete conversion of benzyl alcohol by silent reaction 24 h and the temperature of refluxing solvent ( $\text{CH}_2\text{Cl}_2$ ) are necessary. The proportion of benzaldehyde to benzoic acid was 1:1 under such conditions.

The role of copper sulfate pentahydrate was not specified,<sup>11</sup> but we suppose that it moderates the oxidation power of potassium permanganate, because after 30 min of sono-

chemical oxidation of benzyl alcohol by  $\text{KMnO}_4/\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  just traces of benzoic acid were detected in the reaction mixture. Performing the same sonochemical reaction without support (Table 1, entry 8), conversion of the starting material was complete and the proportion of benzaldehyde to benzoic acid was 38:62.

To improve the selectivity of the oxidation of benzyl alcohol we performed the reaction with 50 and 25% of oxidising agent. As it is possible to see in Table 1, conversion of benzyl alcohol as well as the proportion of the products were not changed when the amount of oxidising agent was lowered to 50%. Further lowering of the amount of oxidising agent to 25% decreased the conversion, but the selectivity of the oxidation was excellent. Benzaldehyde was the only product. No benzoic acid was detected in the reaction mixture even after 2 h of sonochemical reaction and the conversion of benzyl alcohol was 82%.

Improvement of the selectivity was achieved by an argon atmosphere too. After 1.5 h of sonochemical reaction just traces of benzoic acid were detected in the reaction mixture (Table 1, entry 16) while after the same reaction in an air atmosphere 12% of benzoic acid was present in the reaction mixture.

Using TEBA (benzyltriethylammoniumchloride) instead of copper sulfate pentahydrate, conversion of benzyl alcohol increased from 73 to 99% after 0.5 h of sonochemical reaction. On the other hand, the selectivity declined considerably. The proportion of benzoic acid in the mixture of the products increased to 50% as opposed to<sup>1</sup> traces when copper sulfate pentahydrate was used. We found

**Table 1.** Results of the oxidation of benzyl alcohol (**1**) (ultrasonic reaction)

No	Reaction	Time (h)	Conversion (%)	Proportion of <b>2</b> (%)	Proportion of <b>3</b> (%)
1	)))))	0.5	74	>97	Traces
2	)))))	1.0	85	88	12
3	)))))	1.5	100	77	23
4	)))))	2.0	100	55	45
5	)))))	3.0	100	53	47
6	Silent	3.0	<1	–	–
7	Silent	24 <sup>a</sup>	100	50	50
8	)))))	0.5 <sup>b</sup>	100	38	62
9	)))))	0.5 <sup>c</sup>	73	>97	Traces
10	)))))	0.5 <sup>d</sup>	26	100	0
11	)))))	1.0 <sup>d</sup>	47	100	0
12	)))))	1.5 <sup>d</sup>	51	100	0
13	)))))	2.0 <sup>d</sup>	82	100	0
14	)))))	0.5 <sup>e</sup>	99	50	50
15	Silent	0.5 <sup>e</sup>	53	83	17
16	)))))	1.5 <sup>f</sup>	80	>97	Traces

<sup>a</sup> Reaction performed at temperature of refluxed solvent.

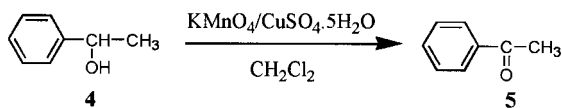
<sup>b</sup> Reaction performed without copper sulfate pentahydrate.

<sup>c</sup> Reaction performed with 50% of oxidising agent.

<sup>d</sup> Reaction performed with 25% of oxidising agent.

<sup>e</sup> Reactions performed with TEBA instead of copper sulfate pentahydrate.

<sup>f</sup> Reaction performed in an argon atmosphere.



Scheme 2.

Table 2. Results of the oxidation of 1-phenylethanol (4)

No	Reaction	Time (h)	Yield of 5 (%)
1	))))	0.5	12
2	))))	1.0	100
3	))))	1.5 <sup>a</sup>	100 (92 <sup>b</sup> )
4	))))	1.0 <sup>c</sup>	52
5	Silent	1.0	8
6	Silent <sup>d</sup>	70	95

<sup>a</sup> Reaction performed with 0.02 mol of 4.

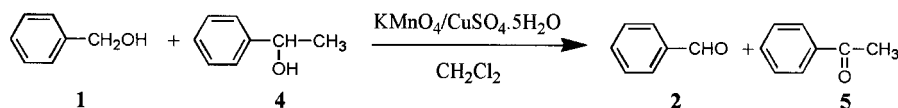
<sup>b</sup> Yield of product isolated after column chromatography.

<sup>c</sup> Reaction performed with 50% of oxidising agent.

<sup>d</sup> Results from literature,<sup>9</sup> temperature of refluxed solvent (CH<sub>2</sub>Cl<sub>2</sub>).

that the conversion of benzyl alcohol in the silent reaction (0.5 h) with KMnO<sub>4</sub> and TEBA was much better (53%) than the conversion in the silent reaction with copper sulfate pentahydrate (<1%, 3 h). The selectivity of the silent reaction was, surprisingly, better than the selectivity of the sonochemical reaction.

Oxidation of a secondary alcohol (Scheme 2) was performed as successfully as oxidation of a primary alcohol. Results of the oxidation of 1-phenylethanol (4) are summarized in Table 2. The sonochemical oxidation gave, after 1 h, 100% of acetophenone (5) while the silent reaction gave after the same time just 8% of acetophenone. Lowering the amount of the oxidising agent to 50% decreased the yield of acetophenone from 100 to 52%. To examine the synthetic utility of this oxidation method, 0.02 mol of 1-phenylethanol was oxidized to acetophenone with very good results. After 1.5 h of sonochemical reaction acetophenone was obtained in quantitative yield.



Scheme 3.

Table 3. Results of the oxidation of the mixture of benzyl alcohol (1) and 1-phenylethanol (4)

No	Reaction	Time (h)	Yield of 2 (%)	Yield of 5 (%)	Proportion 2:5
1	))))	0.25	64	17	3.7:1
2	))))	0.5	67	23	2.9:1
3	))))	0.75	92	40	2.3:1
4	Silent	1.0	15	5	3.0:1
5	))))	1.0 <sup>a</sup>	87 (81 <sup>b</sup> )	22 (17 <sup>b</sup> )	4.0:1
6	))))	0.5 <sup>c</sup>	28	3	9.3:1
7	))))	1.0 <sup>c</sup>	91	25	3.6:1
8	))))	1.0 <sup>d</sup>	80	22	3.6:1
9	))))	2.0 <sup>d</sup>	100	39	2.6:1

<sup>a</sup> Reaction performed with 0.02 mol of starting material (1 and 4).

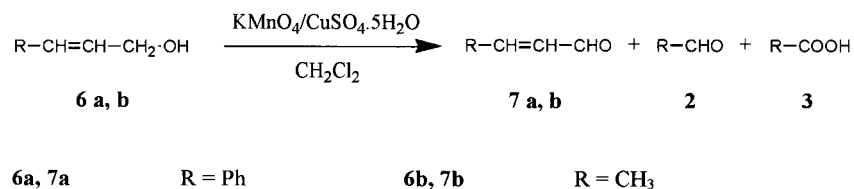
<sup>b</sup> Yield of product isolated after column chromatography.

<sup>c</sup> Reaction performed with 50% of the oxidising agent.

<sup>d</sup> Reaction performed with 25% of the oxidising agent.

Very interesting results were achieved when the equimolar mixture of primary alcohol (benzyl alcohol) and secondary alcohol (1-phenylethanol) was oxidized under the conditions described above (Scheme 3). The results are given in Table 3. The primary alcohol was oxidized more rapidly than the secondary alcohol in all cases. The proportion of conversion of primary alcohol to conversion of secondary alcohol varied from 2.3:1 to 9.3:1 and 92% of primary alcohol and 42% of secondary alcohol were oxidized to corresponding carbonyl compounds after 45 min of sonochemical reaction. On the other hand, after 1 h of silent reaction, only 15% of primary alcohol and 5% of secondary alcohol were oxidized. This selectivity was achieved also when the reaction was performed with 0.02 mol of alcohols (1, 4). During 1 h of sonochemical reaction 87% of benzyl alcohol and 22% of 1-phenylethanol were oxidized according to <sup>1</sup>H NMR analyses. 81% of benzyl alcohol and 17% of 1-phenylethanol were isolated after column chromatography. After lowering the amount of oxidising agent to 50%, conversion decreased, but on the other hand the selectivity increased and 28% of benzylalcohol and 3.3% of 1-phenylethanol only were oxidized to carbonyl compounds after 30 min. Conversion increased after 1 h of sonochemical reaction to 91% in the case of primary alcohol and to 25% in the case of secondary alcohol.

Oxidation of cinnamyl alcohol (6a) gave cinnamaldehyde (7a) and benzaldehyde (Scheme 4) as the main products (Table 4). The proportion of cinnamaldehyde to benzaldehyde in the reaction mixture was 1:1 after 0.5 as well as 1.0 h of the sonochemical reaction. Lowering the amount of the oxidising agent to 50% decreased the conversion from 80 to 19%, but on the other hand the selectivity of the oxidation reaction increased. The proportion of cinnamaldehyde to benzaldehyde was 3:1. In the silent reaction conversion of starting material after 1 h was very low, and just traces of the products were detected by <sup>1</sup>H NMR spectra. On the contrary, oxidation of an unsaturated primary alcohol but-2-ene-1-ol (6b) was selective. The results are



Scheme 4.

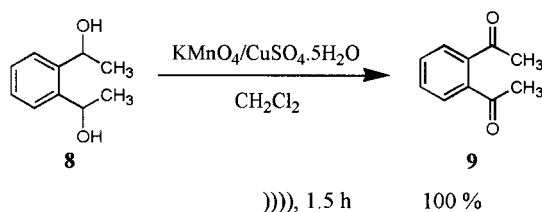
Table 4. Results of the oxidation of **6a** and **6b** (Ultrasonic reaction)

No	R	Reaction	Time (h)	Conversion (%)	Proportion of <b>7</b> (%)	Proportion of <b>2</b> (%)	Proportion of <b>3</b> (%)
1	Ph	))))	0.5	24	56	44	0
2	Ph	))))	1.0	80	51 (45 <sup>a</sup> )	48 (43 <sup>a</sup> )	Traces
3	Ph	))))	1.0 <sup>b</sup>	19	74	26	0
4	Ph	Silent	1.0	<3.0	Traces	Traces	0
5	CH <sub>3</sub>	))))	2.0	8	8	–	–
6	CH <sub>3</sub>	))))	4.0	16	15	–	–
7	CH <sub>3</sub>	Silent	4.0	0	–	–	–

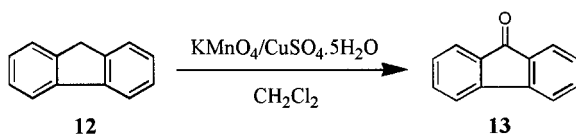
<sup>a</sup> Yield of product isolated after column chromatography.<sup>b</sup> Reaction performed with 50% of the oxidising agent.

shown in Table 4. Conversion of the sonochemical reaction was low –8% after 2 h and 16% after 4 h, respectively. After 4 h of silent reaction starting material only was detected by <sup>1</sup>H NMR analyses of the reaction mixture.

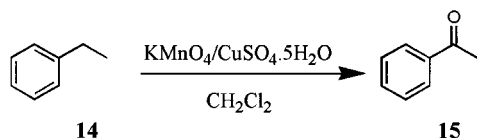
This oxidation method was also successfully used for oxidation of diols and 1,2-bis(1-hydroxyethyl)benzene (**8**) was quantitatively oxidized to 1,2-diacetylbenzene (**9**) after just 1.5 h of sonochemical reaction (Scheme 5).



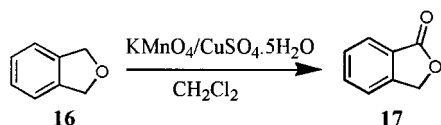
Scheme 5.



Scheme 6.

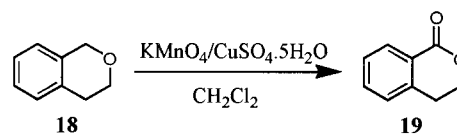


Scheme 7.

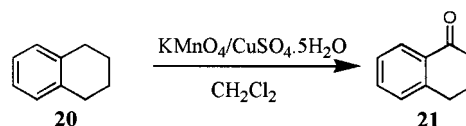


Scheme 8.

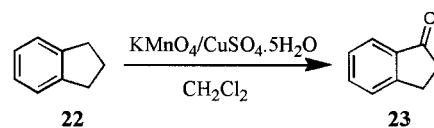
The results of the oxidation of side chains of different alkylaromatic compounds (Schemes 6–13) are summarized in Table 5. Very good yields of oxidation products were achieved after 0.5–4 h of sonochemical reactions at the room temperature (Table 5). The silent reaction under similar conditions gave no or very low yields of the products.



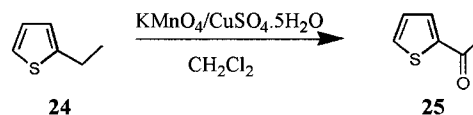
Scheme 9.



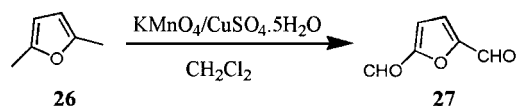
Scheme 10.



Scheme 11.



Scheme 12.



Scheme 13.

**Table 5.** Results of the oxidation of side chains of the alkylarenes (Ultrasonic reaction)

Reactant	Product	Reaction	Time (h)	Yields (%)
Fluorene <b>12</b>	Fluoren-9-one <b>13</b>	)))	2	39
		)))	3	70
		))) <sup>a</sup>	3	26 (25 <sup>b</sup> )
		))) <sup>a</sup>	4	57 (52 <sup>b</sup> )
		Silent	3	0
Ethylbenzene <b>14</b>	1-Phenylethanone <b>15</b>	Silent <sup>c</sup>	48	98
		)))	2	12
		)))	4	40
		))) <sup>a</sup>	4	29 (24 <sup>b</sup> )
		))) <sup>d</sup>	2	4
		))) <sup>d</sup>	4	5
		Silent	4	23
Phthalan <b>16</b>	Phthalide <b>17</b>	Silent <sup>c</sup>	70	95
		)))	1	23
		)))	2	93
		Silent	2	17
		Silent <sup>c</sup>	48	95
Isochromane <b>18</b>	Isochroman-1-one <b>19</b>	)))	0.5	43
		)))	1	76
		)))	2	100
		Silent	2	14
		Silent <sup>c</sup>	72	96
1,2,3,4-tetrahydronaphthalene <b>20</b>	3,4-Dihydronaphthalene-1(2H)-one <b>21</b>	)))	2	41
		)))	3	59
		Silent	3	0
		Silent <sup>c</sup>	72	96
Indane <b>22</b>	Indan-1-one <b>23</b>	)))	2	19
		)))	3	54
		Silent	3	0
		Silent <sup>c</sup>	72	78
		)))	1	33
2-Ethylthiophene <b>24</b>	1-(Thiophen-2-yl) ethanone <b>25</b>	Silent	1	11
2,5-Dimethylfuran <b>26</b>	Furan-2,5-dicarboxaldehyde <b>27</b>	))) <sup>e</sup>	2	8

<sup>a</sup> Reaction performed with 0.02 mol of starting material.

<sup>b</sup> Yield of product isolated after column chromatography.

<sup>c</sup> Results from literature,<sup>9</sup> temperature of refluxed solvent (CH<sub>2</sub>Cl<sub>2</sub>).

<sup>d</sup> Reaction performed with TEBA instead of CuSO<sub>4</sub>·5H<sub>2</sub>O.

<sup>e</sup> Reaction performed with double amount of oxidising agent.

The oxidation took place selectively at the α-position and no cleavage of the C–C bond was observed.

As all experiments were carried out on a very low molar scale we decided to check the synthetic utility of the procedure by an experiment on a 0.02 mol scale. Fluorene (**12**) was chosen as the starting material and as it is possible to see (Table 5) just minor lowering of the yield of the product was observed. Higher conversion of the substrate could be achieved by prolonging the reaction time or by more powerful ultrasonic reactor.

Using TEBA instead of copper sulfate pentahydrate in oxidation of ethylbenzene (**14**) lowered the conversion significantly (Table 5). These results are in contrast to the results of oxidation of benzaldehyde in the presence of TEBA (Table 1).

We can also speculate whether the observed oxidation rate in sonochemical reactions can be caused by some specific ultrasound effect, or it is just due to the effective mass transfer, as is foreseen by Reisse<sup>13</sup> for heterogeneous reactions. We suppose therefore that it would be of interest to study the same reactions using efficient UltraTurax mixers.

## Conclusion

(1) Copper sulfate pentahydrate as a solid support allows the use of KMnO<sub>4</sub> as an oxidant in organic solvents and moderates its oxidation effect; the selective oxidation of benzyl alcohol to benzaldehyde is possible.

(2) Application of ultrasonic irradiation enables significantly shorten reaction times in the heterogeneous oxidations with KMnO<sub>4</sub>/CuSO<sub>4</sub>·5H<sub>2</sub>O as well as lowering the reaction temperature to room temperature. Considerably higher yields of oxidation products were achieved in sonochemical experiments than in similar silent experiments.

## Experimental

All chemical reagents were commercially available. The substrates were purified (distilled or crystallized) before application in the reactions. The <sup>1</sup>H NMR spectra were recorded at 300 MHz on a Varian Gemini spectrometer in CDCl<sub>3</sub> with tetramethylsilane as an internal standard. Conversion of starting material, the yields and the proportion of the products were determined by <sup>1</sup>H NMR. The structure of the products were proved by comparison of

the measured  $^1\text{H}$  NMR spectra with those of commercial standards.

### Preparation of $\text{KMnO}_4/\text{CuSO}_4\cdot 5\text{H}_2\text{O}$

Equal weights of potassium permanganate and copper sulfate pentahydrate were ground together in a mortar until a fine homogeneous powder was obtained.<sup>9</sup>

### General procedure for sonochemical experiments

The substrate (2.8 mmol), dissolved in 40 mL  $\text{CH}_2\text{Cl}_2$ , and oxidant (6.4 g) were irradiated in a glass reactor fitted to an ultrasonic horn JENCONS (20 kHz, 400 W) under pulsed conditions (pulse length: 10 sec; 75% duty) for 0.5–4 h at room temperature under an air atmosphere. After completion, the reaction mixture was filtered through a fritted glass funnel containing a small layer of Celite<sup>®</sup> and the residue was washed with  $\text{CH}_2\text{Cl}_2$  (3×40 mL) and ether (3×40 mL). The solvents were then evaporated in vacuo and the crude product was analyzed by  $^1\text{H}$  NMR spectroscopy and chromatographed on silica gel eluting with isohexane–AcOEt (7:1 and 10:1, respectively). The energy emission of the reactor was measured by the Weissler test:<sup>12</sup> under the conditions used, sonication of aqueous KI (50 mL, 1 M) for 3 min gave 11.0 mol/l of  $\text{KI}_3$ .

### General procedure for silent experiments

The substrate (2.8 mmol), dissolved in 40 mL  $\text{CH}_2\text{Cl}_2$ , and oxidant (6.4 g) were stirred vigorously for 0.5–4 h at room temperature under an air atmosphere. The reaction mixture was then processed as described above.

### Acknowledgements

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