



## Oxone–acetone mediated Wacker-type oxidation of benzo-fused olefins



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### ABSTRACT

Herein we disclose a novel application of the oxone–acetone combination for the Wacker-type oxidation of indenenes and dihydronaphthalenes leading, respectively, to indan-2-ones and 2-tetralones. The amount of the base employed in the reaction seems to switch the reaction path from dioxygenation to Wacker-type oxidation. Control experiments suggest that the reaction is not proceeding via the epoxide route and also that there is no role of trace amounts of metals present in the reagents on the current oxidation.

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Epoxidation, dihydroxylation, and oxidation to ketone are some of the important oxidative transformations of olefins that have been well studied since the beginning of organic synthesis.<sup>1,2</sup> Among these, the oxidation of olefins directly to carbonyl compounds such as aldehydes and ketones has its own industrial and academic significance.<sup>3</sup> The conversion of olefins to carbonyl compounds has been mainly dealt with by employing the complexes of metals such as Hg, Pd, Pt, Au, Ru, and Cu.<sup>4,5</sup> The Wacker oxidation that uses palladium in combination with copper in the presence of an oxidant is one of the most useful and fundamental reactions in organic synthesis.<sup>5</sup> Several modifications have been carried out in recent years that emphasize mainly on the use of green solvents and oxidant free reaction conditions to achieve an effective environment benign method.<sup>6</sup> However, methods that employ less hazardous, cost-effective, and metal free oxidation techniques are still warranted.<sup>7</sup> Herein, we describe a simple metal-free Wacker-type olefin oxidation employing oxone albeit limited mainly to the benzofused olefins such as indenenes and tetralenes.

Oxone is a cheap (comparable with hydrogen peroxide and bleach) and easy to handle reagent. Oxone is endorsed with the ability to oxidize a broad spectrum of functional groups.<sup>8</sup> Very recently, we have shown that the combination of oxone–acetone, which is well established for the olefin epoxidation reactions, can be used for the *cis*-dioxygenation of the benzofused olefins leading to a *cis*-vicinol diol protected as its acetonide.<sup>9</sup> We have come across this unusual dioxygenation accidentally, while carrying out

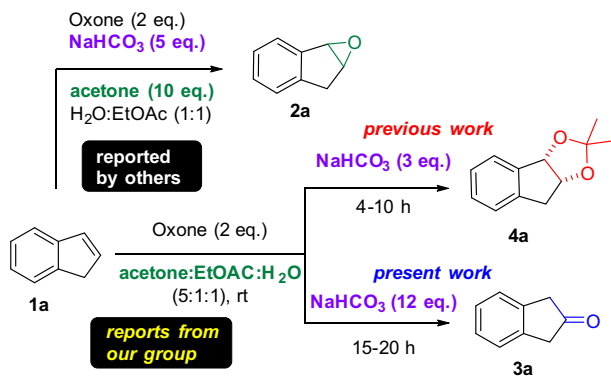
the preparation of the known indene oxide on multi-gram scales employing the oxone–acetone combination for the epoxidation. A set of two side products (2–3%), namely the indan-2-one **3a** and the acetonide **4a** along with the required epoxide **2a** were obtained under the described conditions (Fig. 1).<sup>10</sup> In our previous communication, we have documented a successful realization of the conditions for the direct conversion of indene **1a–4a**. With this, we next looked at the possibility of the Wacker-type oxidation of **1a** leading directly to **3a**.

During our previous investigations on the dioxygenation of **1a**, it has been found that the indan-2-one was isolated as a single product in 35% yield when the oxidation was performed in 0.5 equiv of oxone in the presence of 3 equiv of NaHCO<sub>3</sub> (Table S1 in SI). In order to have a suitable reaction condition for the exclusive formation of 2-indanone, some logical experimentation has been put forward. Optimization experiments have been conducted by varying the proportions of both oxidant and base. The progress and the nature of the intermediates involved in this process have been analyzed with the help of GC–MS. In general, a noticeable change in the consumption of starting material with the product formation was observed with the variation especially in the amounts of base employed (Scheme 1).

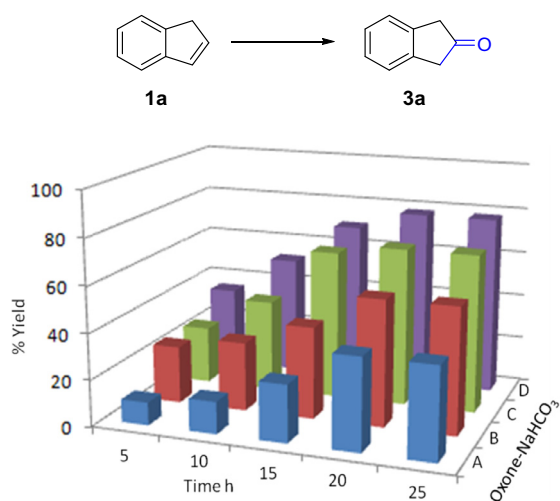
To this end, the use of 12 equiv of NaHCO<sub>3</sub> along with 2 equiv of oxone was found to be the best combination for the complete conversion. Under these optimized conditions, 2-indanone **3a** was obtained in 78% yield at room temperature over the period of 15–20 h. However, no further improvement was observed by increasing the quantity of either oxidant and/or base. Also, prolonging the reaction for longer durations had no effect. Control

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**Figure 1.** Solvent and/or base dependent complementary oxidation of indene with oxone.



**Scheme 1.** Selected conditions explored for the Wacker-type oxidation. Reagents and conditions: All the reactions were carried out at rt with 0.5 mmol of indene in 2.5 ml acetone and 0.5 ml of (1:1 of H<sub>2</sub>O + EtOAc); (A) oxone (0.5 equiv), NaHCO<sub>3</sub> (3 equiv); (B) oxone (1.0 equiv), NaHCO<sub>3</sub> (6 equiv); (C) oxone (1.5 equiv), NaHCO<sub>3</sub> (9 equiv); (D) oxone (2.0 equiv), NaHCO<sub>3</sub> (12 equiv).

experiments revealed that the acetone/H<sub>2</sub>O/EtOAc (5:1:1) employed for *syn*-dioxygenation was also found to be the best solvent combination system for the current Wacker-type oxidation. The optimized reaction conditions involve the addition of 2 equiv of powdered oxone to a stirred slurry of 12 equiv of NaHCO<sub>3</sub> and 1 equiv indene in a mixture of solvents (5:1:1 acetone/water/ethyl acetate) stirred at room temperature over the prescribed time. The oxidation of simple indene **1a** under this condition provided the required **3a** in 78% yield as the sole product in 18 h.

The scope of this reaction has been generalized by employing various substituted indene derivatives **1b–1h**. In general, the reactions proceeded smoothly and provided exclusively corresponding 2-indanones in good yields. As shown in Table 1, the substitution at the C3 (**1b–1g**) and at C1 position (**1h**) of indene has little effect on the outcome of the reaction (in terms of yields and the regioselectivity) and proceeded smoothly. This suggested that the reaction is highly regioselective in nature. As expected, the C-1 substituted indene **1h** (1-benzyl-1*H*-indene) and the C-3 substituted **1g** (3-benzyl-1*H*-indene) led to the formation of 1-benzyl-1*H*-inden-2(3*H*)-one (**3g**). Gratifyingly, the reaction conditions

**Table 1**  
Scope of oxone–acetone mediated Wacker-type oxidation of indene derivatives<sup>a</sup>

Entry	Substrate	Product	Yield <sup>b</sup> (%)
1	<b>1b</b>	<b>3b</b>	70
2	<b>1c</b>	<b>3c</b>	74
3	<b>1d</b>	<b>3d</b>	74
4	<b>1e</b>	<b>3e</b>	72
5	<b>1f</b>	<b>3f</b>	61
6	<b>1g</b>	<b>3g</b>	75
7	<b>1h</b>	<b>3g</b>	78
8	<b>1i</b>	<b>3i</b>	71
9	<b>1j</b>	<b>3j</b>	65
10	<b>1k</b>	<b>3k</b>	61
11	<b>1l</b>	<b>3l</b>	76
12	<b>1m</b>	<b>3m</b>	70
13	<b>1n</b>	<b>3n</b>	72

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