

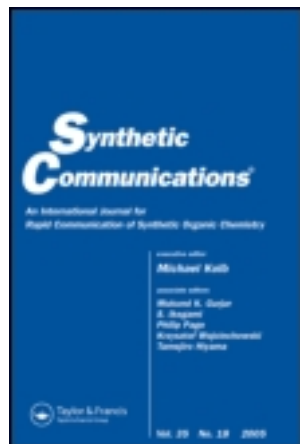
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## Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lcyc20>

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Published online: 10 Dec 2007.

To cite this article: Digambar D. Gaikwad, Satish A. Dake, Ravibhushan S. Kulkarni, Wamanrao N. Jadhav, Shankar B. Kakde & Rajendra P. Pawar (2007) Efficient Baeyer-Villiger Oxidation of Ketones using Molecular Iodine/H<sub>2</sub>O<sub>2</sub> as Heterogeneous Catalytic System, *Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry*, 37:23, 4093-4097, DOI: [10.1080/00397910701572589](https://doi.org/10.1080/00397910701572589)

To link to this article: <http://dx.doi.org/10.1080/00397910701572589>

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## Efficient Baeyer–Villiger Oxidation of Ketones using Molecular Iodine/H<sub>2</sub>O<sub>2</sub> as Heterogeneous Catalytic System

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**Abstract:** The use of molecular iodine as a catalyst for the oxidation of ketones using hydrogen peroxide in the presence of acetic acid at room temperature is reported.

**Keywords:** acetic acid, ketones, hydrogen peroxide, molecular iodine

### INTRODUCTION

Baeyer–Villiger oxidation of ketones is an important tool in ester/lactone synthesis. The reaction was first reported for the conversion of cyclic

Received May 3, 2007

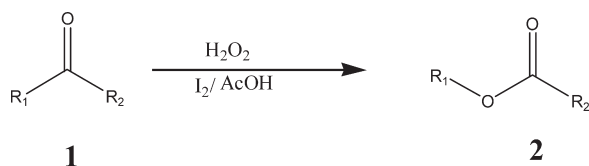
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ketones to the corresponding lactones using Caro's acid.<sup>[1]</sup> The use of Baeyer–Villiger oxidation in several stereoselective organic syntheses is known.<sup>[2,3]</sup> Baeyer–Villiger oxidation has been studied in the presence of trifluoroacetic acid, and perbenzoic acid, and meta-chloroperbenzoic acid, which produces a large amount of waste.<sup>[3,4]</sup> Several other catalysts are also reported, such as heterogeneous catalysts based on solid acid,<sup>[5]</sup> zeolites,<sup>[6]</sup> titanium silicate,<sup>[7]</sup> Se,<sup>[8]</sup> arsenic (As),<sup>[9]</sup> and homogeneous catalysts based on platinum (Pt),<sup>[10]</sup> zirconium (Zr),<sup>[11]</sup> rhenium (Re),<sup>[12]</sup> selenium (Se),<sup>[13]</sup> As,<sup>[14]</sup> and molybdenum (Mo).<sup>[15]</sup> The oxidation was also studied with molecular oxygen catalyzed by a metal complex or supported metal complex.<sup>[16]</sup> A selective oxidation is also known to oxidize the substrate by activating the  $>C=O$  group of the lactones instead of  $H_2O_2$  activation using Sn/Zeolite catalyst.<sup>[17]</sup>

The use of molecular iodine in several organic synthesis reactions attracted considerable attention because it is a nontoxic, readily available, inexpensive, and mild Lewis acid catalyst. The molecular iodine used in several organic transformations, such as synthesis of benzothiophenes<sup>[18]</sup> and bis-indoles,<sup>[19]</sup> deprotection of acetals,<sup>[20]</sup> esterification,<sup>[21]</sup> transesterification,<sup>[22]</sup> and Michael addition.<sup>[23]</sup> Recently, the use of iodine for the synthesis of  $\beta$ -keto-enol esters<sup>[24]</sup> and multicomponent dihydropyrimidinone synthesis<sup>[25]</sup> also has been reported.

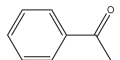
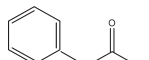
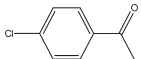
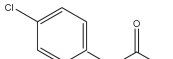
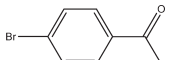
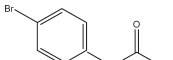
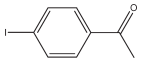
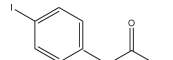
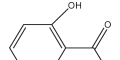
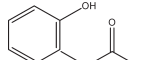
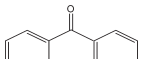
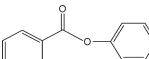
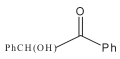
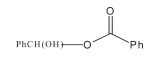







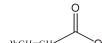
In a typical procedure, to a mixture of molecular iodine and 40% hydrogen peroxide in acetic acid acetophenone in acetic acid was added. The mixture was stirred at room temperature for 1 h. The progress of the reaction was checked by thin-layer chromatography (TLC, hexane–ethyl acetate 8:2). After completion of the reaction, an aqueous workup afforded the corresponding ester. To evaluate the use of this procedure, different ketones were oxidized. The reaction proceeded very cleanly at room temperature, and no undesirable side reactions were observed. In the absence of molecular iodine catalyst, the reaction did not proceed, even after 10 h (Scheme 1).

We have demonstrated an efficient and mild protocol for the oxidation of different ketones to give corresponding esters at room temperature in acetic acid using a catalytic amount of molecular iodine in excellent yields (Table 1). Similarly, the aldehydes using the same procedure afforded corresponding acids in 12 h of stirring at room temperature.



**Scheme 1.**  $R_1$  and  $R_2 = \text{H}/\text{Alkyl}/\text{Aryl}$ .

**Table 1.** Baeyer–Villiger oxidation in the presence of H<sub>2</sub>O<sub>2</sub> and AcOH-I<sub>2</sub>

Entry	Substrate (1)	Product (2)	Time	Yield (%)
1			1 h	80
2			15 min	90
3			35 min	85
4			10 min	95
5			20 min	90
6			10 min	93
7			1 h	80
8			1 h	85
9			1 h	70
10			12 h	50
11			12 h	50

## EXPERIMENTAL

All the melting points were determined in open capillaries and are uncorrected. TLC routinely checked the purity of the synthesized esters on silica-gel-coated plates.

### Preparation of Phenyl Acetate

To a mixture of molecular iodine (50 mg), hydrogen peroxide (40%, 4 ml, 0.117 mol), and acetic acid (0.5 ml, 0.016 mol) was added. The mixture was stirred for half an hour at room temperature. Acetophenone (2 ml, 0.0188 mol) in 3 ml of acetic acid was added to the mixture and stirred for 1 h at room temperature. The progress of the reaction was checked by TLC

(hexane–ethyl acetate 8:2). After completion of the reaction, the mixture was poured on ice-cooled water. The reaction mixture was extracted with  $4 \times 25$  ml diethyl ether. The organic layer was dried over anhydrous sodium sulphate and the ether was evaporated under vacuum to afford the crude product. The obtained crude product was further purified by column chromatography using hexane–ethyl acetate 8:2 as an eluent. Yield = 80%.

The products obtained were identified by comparing data with authentic samples, TLC,  $^1\text{H}$  NMR, and IR spectral spectroscopy.

### Data

**Entry 1:** IR ( $\text{cm}^{-1}$ ) 3062, 2850, 1685, 1444, 1263, 1178, and 1080.  $^1\text{H}$  NMR 2.59 $\delta$  (3H, s,  $\text{CH}_3$ ), 7.4–7.6 $\delta$  (3H, m, Ar-H), 7.9–8.0 $\delta$  (2H, d, Ar-H).

**Entry 2:** IR ( $\text{cm}^{-1}$ ) 3068, 2845, 1685, 1484, 1261, 1182, and 1050.  $^1\text{H}$  NMR 2.56 $\delta$  (3H, s,  $\text{CH}_3$ ), 7.38 $\delta$  (2H, d, Ar-H), 7.80 $\delta$  (2H, d, Ar-H).

### ACKNOWLEDGMENTS

The authors are thankful to P. L. More, principal, Dnyanopasak College, Parbhani, for providing the necessary facilities.

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