

Chiral Brønsted Acid Catalyzed Asymmetric Baeyer–Villiger Reaction of 3-Substituted Cyclobutanones by Using Aqueous H₂O₂**

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The Baeyer–Villiger (BV) reaction represents one of the most well-known and widely applied reactions in organic synthesis.^[1] Although more than one century has gone by since its discovery in 1899,^[2] the BV reaction is still far from being fully developed. Although the use of aqueous hydrogen peroxide as an environmentally benign oxidant has been a long-sought goal for the BV reaction,^[3] significant efforts still need to be made in the area of enantioselective BV reactions. Since the pioneering work by the groups of Strukul^[4a] and Bolm^[4b] in 1994, a number of chiral metal complexes or organic molecules have been developed as promoters or catalysts for the BV reaction of various ketones,^[5] but there are only a few cases in which the catalysts are used in combination with aqueous hydrogen peroxide as the oxidant.^[4a,6] Although very impressive results have been achieved for the catalytic enantioselective BV reaction in the work reported by the groups of Bolm,^[4b,7] Katsuki,^[8] and Murahashi,^[6b] the development of the reaction is slow when compared to the rapid development of other catalytic asymmetric transformations.^[9] To the best of our knowledge only a few catalyst systems afford products from the BV oxidation of 3-substituted cyclobutanones in more than 80 % *ee*,^[8b,c] despite the fact that some enzymatic systems show excellent enantiocontrol in the reaction.^[10] Herein, we communicate our preliminary results on the first example of the enantioselective BV oxidation of 3-substituted cyclobutanones catalyzed by a chiral Brønsted acid and 30 % aqueous H₂O₂ as the oxidant to afford the corresponding γ -lactones in excellent yields and up to 93 % *ee*.

The research was inspired by the fact that BV reaction is accelerated by strong Brønsted acids, and that the activity of the peracid is dependent on the acidity of the Brønsted acid.^[3,11] It was reported that the use of a stoichiometric amount of the chiral organic hydroperoxide {(4*R*,5*R*)-5-[(hydroperoxydiphenyl)methyl]-2,2-dimethyl-1,3-dioxolan-4-yl}diphenylmethanol (TADOOH) afforded enantioselectivities of 55 % in the asymmetric BV oxidation of bicyclo-[4.2.0]octanone.^[12] The difficulty in developing a catalytic enantioselective version of this reaction may be ascribed to the weak acidity of the hydroxy groups in the $\alpha,\alpha,\alpha',\alpha'$ -tetraaryl-1,3-dioxolan-4,5-dimethanol (TADDOL) molecule. Chiral phosphoric acids derived from 2,2'-dihydroxy-1,1'-binaphthyl (binol) are recognized as Brønsted acids that are widely used as catalysts in a variety of asymmetric reactions with high catalytic activity and excellent enantioselectivity.^[13] A preliminary examination of binol-derived phosphoric acid **1a** (10 mol %) in the BV oxidation of 3-phenylcyclobutanone (**2a**) with 1.5 equivalents of aqueous H₂O₂ (30 %) in CHCl₃ at room temperature afforded 3-phenyl- γ -butyrolactone (**3a**) with good catalytic activity (12 h, 99 % yield), albeit very poor enantioselectivity (ca. 2 % *ee*). Notably, a reaction did not occur in the absence of **1a** under otherwise identical experimental conditions. These results clearly showed the accelerating effect of the phosphoric acid in the BV oxidation of cyclobutanone and prompted us to improve the catalytic performance of the phosphoric acids by tuning the steric and electronic properties of 3,3' substituents and the backbone of the scaffold (Figure 1). Both the catalytic efficiency and asymmetric induction are strongly dependent on the solvents used. Among the variety of solvents examined for the

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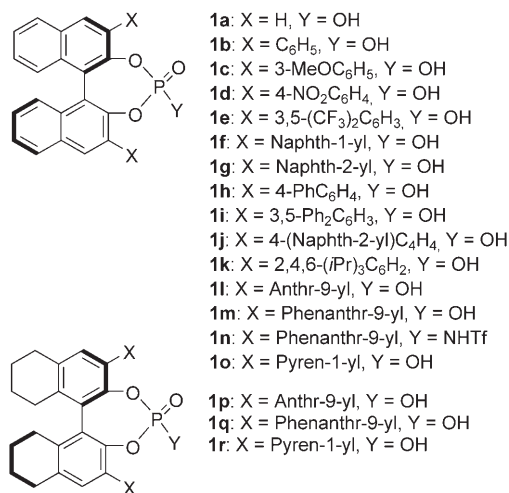
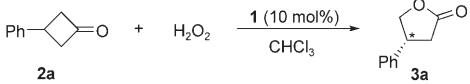


Figure 1. Binol- and H₈-binol-derived phosphoric acids **1a–r**.

catalysis, chloroform is the best choice in terms of the enantioselectivity (see the Supporting Information; Table S1).

In most cases the reaction of **2a** proceeds smoothly in chloroform to give corresponding lactone (*R*)-**3a** in good to excellent yields (Table 1). Changes in the substituents at the

Table 1: BV oxidation of 3-phenylcyclobutanone with H₂O₂ catalyzed by various phosphoric acids.^[a]

				
Entry	Cat.	<i>t</i> [h]	Yield [%] ^[b]	<i>ee</i> [%] ^[c]
1	1b	24	99	12
2	1c	24	72	16
3	1d	12	99	18
4	1e	12	99	12
5	1f	24	94	29
6	1g	24	72	37
7	1h	24	82	34
8	1i	24	72	23
9	1j	24	29	13
10	1k	24	99	37
11	1l	24	85	44
12	1m	24	72	54
13	1n	12	99	5
14	1o	24	73	57
15	1p	24	89	50
16	1q	24	91	65
17	1r	24	95	71
18	1r	48	88	78 ^[d]
19	1r	43	65	88 ^[e]
20	1r ^[f]	18	99	88 ^[e]

[a] The reaction was carried out at room temperature with **[2a]** = 0.1 M. **3a** was confirmed to have an absolute configuration of *R* by comparison of its optical rotation to that reported in the literature.^[6b] [b] Yield of isolated product. [c] The enantiomeric excess of **3a** was determined by HPLC analysis with a chiral column (Chiralpak AS-H). [d] The reaction was carried out at 0 °C. [e] The reaction was carried out at –40 °C. [f] Catalyst **1r** was washed with 4 N HCl and water prior to use.

3,3'-positions of the binaphthyl catalyst scaffold significantly affect the enantioselectivities of the reaction; for example, the introduction of a variety of substituted phenyl moieties resulted in enantioselectivities ranging from 12 % to 37 % (Table 1, entries 1–4 and 7–10). The phosphoric acid with naphth-2-yl substituents (**1g**) is superior to that having naphth-1-yl substituents (**1f**) in terms of enantioselectivity (Table 1, entry 5 versus 6). The fused aromatic substituents, such as anthr-9-yl, phenanthr-9-yl, or pyren-1-yl groups, at the 3,3'-positions of the phosphoric acids (**1l**, **1m**, and **1o**) are favorable for the control of the enantioselectivity (Table 1, entries 11, 12, and 14). The pyren-1-yl-substituted acid (**1o**) demonstrates the best enantioselectivity and affords product (*R*)-**3a** in 57 % *ee*. Although an analogous *N*-triflyl phosphoramidate (**1n**) demonstrated excellent catalytic activity in the BV oxidation of **2a**, the enantioselectivity of the reaction is only modest (5 % *ee*, Table 1, entry 13). Investigation of the backbone effect of the binaphthyl skeleton indicated that all H₈-binol-derived (H₈-binol = 5,5',6,6',7,7',8,8'-octahydro-1,1'-

bi-2-naphthol)phosphoric acids (**1p**, **1q**, and **1r**) generally showed higher enantioselectivities (Table 1, entries 15–17) than their corresponding binol-derived analogues in the catalysis of the BV reaction of **2a** (Table 1, entries 11, 12, and 14). (*R*)-**3a** was obtained in up to 71 % *ee* at room temperature with catalyst **1r**, which features pyren-1-yl groups at the 3,3'-positions of the catalyst. The impact of steric and electronic properties of the 3,3' substituents and the effect of the backbone of phosphoric acid scaffold on the enantioselectivities of the reaction show that fine tuning of the chiral environment around phosphoric acid is critical for the enantioselectivity of the reaction.

The effect of temperature on the enantioselectivity of the catalysis is also remarkable. The enantiomeric excess of product **3a** can be improved to 78 % when the reaction temperature is reduced to 0 °C (Table 1, entry 18), and the *ee* value can be enhanced to 88 % when the reaction is carried out at –40 °C (Table 1, entry 19). Notably, this value represents the highest enantioselectivity attained in catalytic asymmetric BV oxidation of **2a** with chemical catalysts.^[1–8] Interestingly, when catalyst **1r** was washed with 4 N HCl and water prior to use, its activity was significantly improved without loss of enantioselectivity (Table 1, entry 20). The exact reason for the improvement of the activity is not yet clear, but it might be attributed to the removal of some trace amounts of impurities that poison the catalyst.

A variety of 3-aryl- or alkyl-substituted cyclobutanones can be enantioselectively oxidized by using 10 mol % of catalyst **1r** with 1.5 equivalents of aqueous H₂O₂ (30 %) as the oxidant under the optimized reaction conditions (Table 2). Good to excellent enantioselectivities (82–93 % *ee*) were

Table 2: Asymmetric BV oxidation of 3-substituted cyclobutanones with H₂O₂ catalyzed by **1r**.^[a]

Reaction scheme showing the conversion of 3-substituted cyclobutanone (**2a-j**) to 3-substituted lactone (**3a-j**) using **1r** (10 mol%) in CHCl_3 at -40°C with H_2O_2 .

Entry	R	R'	<i>t</i> [h]	Yield [%] ^[b]	<i>ee</i> [%] ^[c] (Conf.) ^[d]
1	C ₆ H ₅ (a)	H	18	99	88(<i>R</i>)
2	4-MeC ₆ H ₄ (b)	H	18	99	93(<i>R</i>)
3	4-MeOC ₆ H ₄ (c)	H	18	99	85(<i>R</i>)
4	4-BrC ₆ H ₄ (d)	H	18	99	83(<i>R</i>)
5	4-ClC ₆ H ₄ (e)	H	18	99	82(<i>R</i>)
6	4-FC ₆ H ₄ (f)	H	18	99	84(<i>R</i>)
7	2-naphthyl (g)	H	18	91	86(<i>R</i>)
8 ^[e]	4-MeC ₆ H ₄ (b)	H	80	95	93(<i>R</i>)
9	C ₆ H ₅ CH ₂ (h)	H	18	99	58(<i>S</i>)
10	4-MeOC ₆ H ₄ CH ₂ (i)	H	18	99	57(<i>S</i>)
11	3,4-(MeO) ₂ C ₆ H ₃ CH ₂ (j)	H	36	99	55(<i>S</i>)
12	C ₆ H ₅ (k)	CH ₃	24	99	(+)-61 (n.d.) ^[f]

[a] All the reactions were carried out at –40 °C with **[2]** = 0.1 M. [b] Yield of **3** (isolated). [c] The *ee* values of **3a–k** were determined by HPLC analysis with a Daicel chiral column (see the Supporting Information). [d] The absolute configurations of **3** were confirmed by comparison of the optical rotations with those reported in the literature^[6b] or deduced by comparison of the Cotton effects in CD spectra with those of analogous authentic compounds (see the Supporting Information, Figures S2 and S3). [e] Catalyst loading was 1 mol %. [f] Absolute configuration was not determined.

obtained for the reaction of aryl-substituted cyclobutanones (Table 2, entries 1–7), which were higher than those achieved with alkyl-substituted cyclobutanones (55–58% *ee*; Table 2, entries 9–11). The cyclobutanone bearing a 4-tolyl group was converted into corresponding lactone (*R*)-**3b** in near quantitative yield and 93% *ee* (Table 2, entry 2); this represents the first example of a highly enantioselective BV oxidation of 3-substituted cyclobutanone with greater than 90% *ee*. When the catalyst loading was reduced to 1 mol% and the reaction time extended to 80 hours, (*R*)-**3b** was obtained in 95% yield with same enantioselectivity (93% *ee*) (Table 2, entry 8). Excellent reactivity was also observed in the reaction of 3,3-disubstituted cyclobutanone, albeit with moderate enantioselectivity (61% *ee*, Table 2, entry 12).

To gain insight into the mechanism of the present asymmetric induction process, we first studied the nonlinear effects^[14] of the reaction to provide some information on the nature of the catalytic species. The investigation showed that the *ee* values of the product are proportional to those of the catalyst (see the Supporting Information, Figure S1). Moreover, the change of concentration of catalyst **1m** from 0.02 M to 0.003 M (at 10 mol% loading relative to the substrate) at room temperature does not have a substantial impact on the enantioselectivity (51–55% *ee*) of the reaction (see the Supporting Information, Table S3). All these facts suggest that the transition state of the present catalytic system does not involve two or more molecules of the catalyst.^[11c,15] On the basis of the absolute configuration observed for the products, the commonly accepted mechanism for BV reaction,^[3,16] and the preferential conformation of the Criegee intermediate in the chiral environment provided by the catalyst, a plausible working model for asymmetric induction in the present catalytic system is proposed in Figure 2.

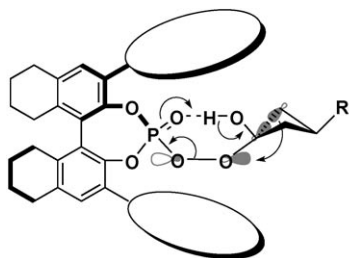


Figure 2. Proposed working model for the asymmetric induction in the BV oxidation of 3-substituted cyclobutanone catalyzed by a chiral phosphoric acid.

The nucleophilic attack of the peracid onto the polarized C=O bond forms the Criegee adduct, which undergoes intramolecular migration by the interaction of an σ -orbital of one C–C bond with the σ^* -orbital of the O–O bond. Simultaneous intramolecular migration of the hydroxy proton within the intermediate structure through a H $\cdots$ O=P interaction affords the corresponding lactone product and regenerates the phosphoric acid catalyst. According to the generally accepted transition-state model^[16–18] the migrating carbon atom needs to be antiperiplanar to both the O–O bond of the leaving group and the lone pair of electrons of the

hydroxy group. Therefore, the sense of asymmetric induction is determined by the conformation of the Criegee intermediate and its subsequent rearrangement. The preferential conformation of the Criegee intermediate is dictated by the chiral environment generated by the 1,1'-bi-2-naphthyl backbone and the bulky 3,3'-pyren-1-yl moieties. As shown in Figure 2, the intramolecular rearrangement occurs to give the (*R*)- γ -butyrolactone (*R* = aryl group).

In conclusion, chiral phosphoric acids have been found to catalyze the enantioselective BV oxidation of a variety of 3-substituted cyclobutanones with aqueous H₂O₂ (30%) as the oxidant to afford the corresponding γ -lactones in excellent yields and up to 93% *ee*. On the basis of the observed absolute configurations in the products and the proportional relationship between the *ee* values of the product and the catalyst, a plausible model for asymmetric induction was proposed. This work is the first demonstration of a strong chiral Brønsted acid catalyzing an asymmetric BV transformation, and will probably lead to additional development of the environmentally benign process. Additional research on the mechanism of the asymmetric induction and the extension of the methodology to other types of oxidations are underway in our laboratory.

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