

# RSC Advances



This article can be cited before page numbers have been issued, to do this please use: Z. Wang, H. Zhang, D. Dong and S. Hao, *RSC Adv.*, 2016, DOI: 10.1039/C5RA27500H.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



## Journal Name

## COMMUNICATION

Bu<sub>4</sub>Ni-catalyzed construction of *tert*-butyl peresters from alcoholsHui Zhang,<sup>a1</sup> Dao-Qing Dong,<sup>a1</sup> Shuang-Hong Hao<sup>a</sup> and Zu-Li Wang<sup>a\*</sup>Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

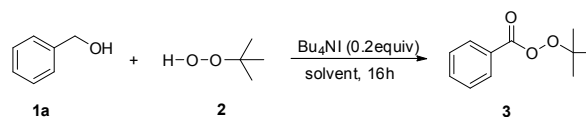
**A new method for the synthesis of *tert*-butyl peresters directly from available alcohols catalyzed by Bu<sub>4</sub>Ni at room temperature in aqueous system was developed. Additionally, allylic esters could also be obtained by combing this method and Kharasch–Sosnovsky reaction via a two-step one-pot procedure.**

The synthesis of *tert*-butyl peresters is an important task to the research community due to their importance as core structure in organic chemistry.<sup>1</sup> However, the method for the synthesis of *tert*-butyl peresters are limited. Traditionally method for the synthesis of *tert*-butyl peresters relied on the reaction of carboxylic acid and its derivative with *tert*-butyl hydroperoxide.<sup>2</sup> In 2011, an alternative method for the synthesis of *tert*-butyl peresters from aldehydes was disclosed Wan *etc.*<sup>3</sup> However, versatile and practical methods for the synthesis of *tert*-butyl peresters are still desirable.

Tetrabutylammonium Iodide (TBAI) in combination with *tert*-butyl hydroperoxide (TBHP) has been recognized as high effective and environmentally benign catalyst in most coupling and radical reactions in recent years.<sup>4</sup> For example, construction of C–O,<sup>5</sup> C–N,<sup>6</sup> C–C<sup>7,4f</sup> bonds through cross-dehydrogenation coupling (CDC) reaction catalysed by TBAI have been well established. In continuation of our interests in green chemistry,<sup>8</sup> herein, we disclose the synthesis of *tert*-butyl peresters from the reaction of alcohols with TBHP using Bu<sub>4</sub>Ni as the catalyst.

At the beginning of our studies, a model reaction of phenylmethanol and TBHP was chosen for optimization of the reaction conditions. It was found that the solvent can greatly effect the yield of the reaction. When water was used as solvent, the highest yield of the desired product was obtained (table 1, entry 1). High yield was also obtained when DMF was used (table 1, entry 2). However, other solvents such as DMSO,

toluene, CH<sub>3</sub>OH *etc.* showed lower yields (table 1, entries 3–6). Further study indicated that other catalysts including KI, CuI, FeCl<sub>2</sub> *etc.* lead to relatively low yields. (table 1, entries 7–14). When the reaction time was reduced to 12h, a lower yield of the product was obtained (table 1, entry 15). However, prolonging the reaction time showed almost the same yield (table 1, entry 16). The effect of the temperature on the reaction was also investigated. Decreasing the reaction temperature to RT led to a slightly lower yield (table 1, entry 17). But there was no significant changes on the yield when

Table 1. Optimization of the Reaction Conditions<sup>a</sup>

Entry	Catalysts	Solvent	t (h)	T (°C)	Yield (%)
1	Bu <sub>4</sub> Ni	H <sub>2</sub> O	16	40	98
2	Bu <sub>4</sub> Ni	DMF	16	40	83
3	Bu <sub>4</sub> Ni	DMSO	16	40	40
4	Bu <sub>4</sub> Ni	CH <sub>3</sub> OH	16	40	39
5	Bu <sub>4</sub> Ni	Toluene	16	40	64
6	Bu <sub>4</sub> Ni	EG	16	40	50
7	KI	H <sub>2</sub> O	16	40	68
8	CuI	H <sub>2</sub> O	16	40	67
9	CuCl <sub>2</sub>	H <sub>2</sub> O	16	40	30
10	FeCl <sub>2</sub>	H <sub>2</sub> O	16	40	32
11	FeCl <sub>3</sub>	H <sub>2</sub> O	16	40	31
12	I <sub>2</sub>	H <sub>2</sub> O	16	40	40
13	Bu <sub>4</sub> NiCl	H <sub>2</sub> O	16	40	35
14	CuBr	H <sub>2</sub> O	16	40	28
15	Bu <sub>4</sub> Ni	H <sub>2</sub> O	12	40	80
16	Bu <sub>4</sub> Ni	H <sub>2</sub> O	24	40	97
17	Bu <sub>4</sub> Ni	H <sub>2</sub> O	16	RT	95
18	Bu <sub>4</sub> Ni	H <sub>2</sub> O	16	60	97

<sup>a</sup> College of Chemistry and Pharmaceutical Sciences, Qingdao Agricultural University, Qingdao, 266109, P. R. China. E-mail: wangzulichem@163.com.

† Footnotes relating to the title and/or authors should appear here.

<sup>1</sup> These authors contributed equally to this article

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

## COMMUNICATION

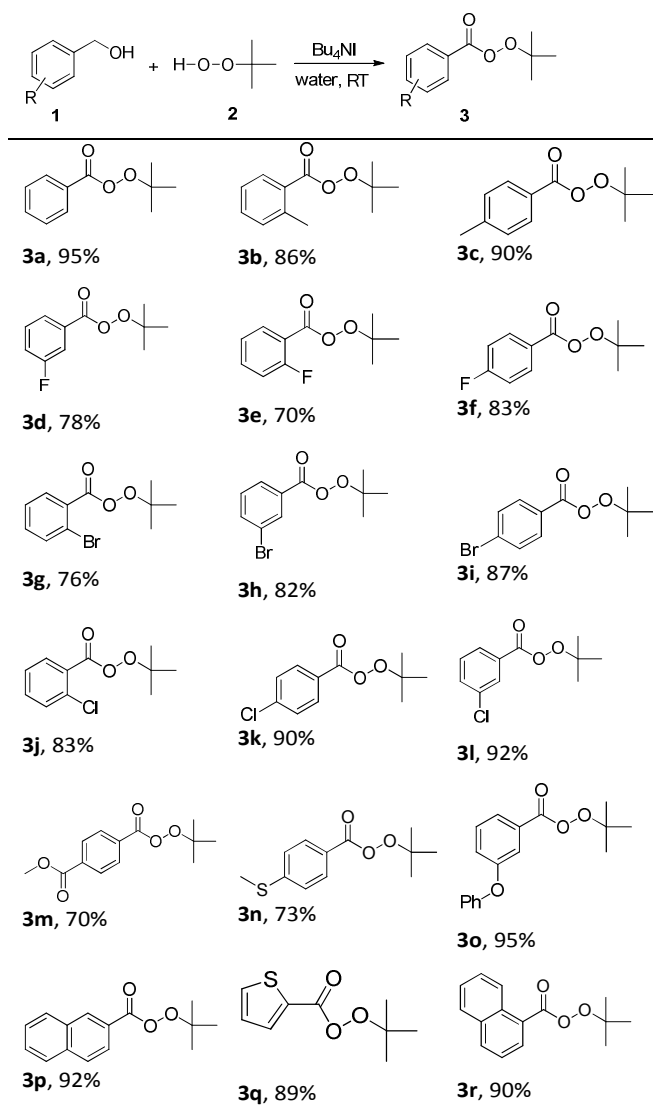
Journal Name

<sup>a</sup> Reaction conditions: 1a (0.5 mmol), 2 (2.5 mmol), TBAI (0.25 mmol), solvent (2 mL), 16 h. Isolated yields. EG: ethylene glycol

the reaction temperature was elevated to 60 °C (table 1, entry 18).

After completion of the search for the optimized reaction conditions, we chose a variety of structurally diverse phenylmethanol possessing a wide range of functional groups to understand the scope and generality of the reaction. It

**Table 2** Synthesis of *tert*-butyl peresters catalysed by Bu<sub>4</sub>NI<sup>a</sup>



<sup>a</sup> Reaction conditions: 1 (0.5 mmol), 2 (2.5 mmol), Bu<sub>4</sub>NI (20 mol%), water (2 mL), RT, 16 h. Isolated yield.

should be noted that a variety of functional groups, including methyl, ether, sulfide, halide and ester ran well in this reaction. Because of smaller hindrance of 4-substituted phenylmethanol and 3-substituted phenylmethanol compared with its analogues 2-substituted phenylmethanol, 4-substituted

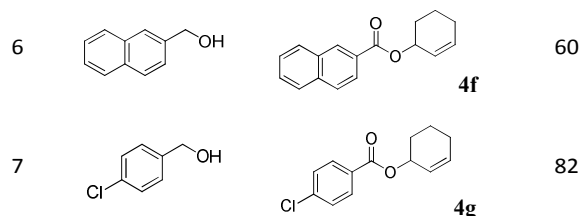
phenylmethanol and 3-substituted phenylmethanol gave a higher yield than that of 2-substituted phenylmethanol (table 2, **3d-3l**). Additionally, naphthalen-1-ylmethanol and naphthalen-2-ylmethanol were also good substrates in this reaction affording the desired products in high yield (table 2, **3p**, **3r**). Heteroarenes, thiophen-2-ylmethanol could also providing the corresponding product in high yields (table 2, **3q**). It is interesting to note that when aliphatic alcohols 2-(4-methoxyphenyl)ethanol was subjected to this reaction, *tert*-butyl 4-methoxybenzoperoxoate (**3s**) was obtained in 36% yield (Scheme 1). A decarbonylation process may occurred in this reaction. However, other aliphatic alcohols such as 2-(4-chlorophenyl)ethanol, 2-phenylethanol were not suitable for this reaction. The same excellent results were also obtained when this method was performed at a gram scale using (4-chlorophenyl)methanol as substrate (Scheme 2). This example clearly demonstrates the preparative utility of this newly developed method.

To investigate the synthetic application of the methodology in organic synthesis. The Kharasch–Sosnovsky reaction between the *tert*-butyl peresters and cyclohexene was conducted in two-step one-pot process. As it was shown in table 3, both electron-withdrawing groups (F, Br, Cl) (table 3, **4a**, **4b**, **4g**) and electron-donating groups (CH<sub>3</sub>S, PhO) (table 3, **4c**, **4e**) are all well tolerated in this system. Besides substituted phenylmethanol, thiophen-2-ylmethanol and naphthalen-2-ylmethanol (table 3, **4d**, **4f**) also worked well in this system.

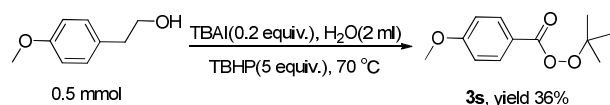
**Table 3** Synthesis of allylic ester in two-step one-pot process<sup>a</sup>

Reaction scheme for Table 3: Phenylmethanol (1) reacts with cyclohexene in a two-step one-pot process: (1) Bu<sub>4</sub>NI, TBHP, CH<sub>2</sub>Cl<sub>2</sub>, RT; (2) 5mol % CuBr, cyclohexene to form allylic ester (4).

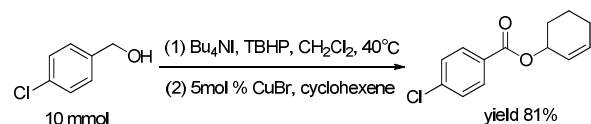
Entry	Substrate 1	Product 4	Yield (%)
1			80
2			76
3			73
4			85
5			79



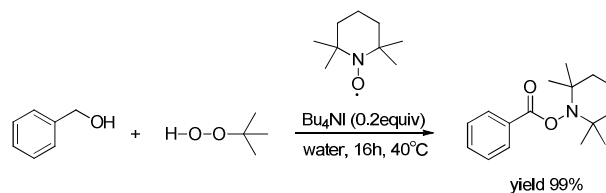
<sup>a</sup> Step 1: **1** (0.5 mmol), **2** (2.5 mmol), Bu<sub>4</sub>Ni (20 mol%), CH<sub>2</sub>Cl<sub>2</sub> (2 mL), RT, 16 h.; step 2: CuBr (5 mol%), cyclohexene (10 equiv.), 40 °C for 36 h.



**Scheme 1** Reactions between aliphatic alcohol 2-(4-methoxyphenyl)ethanol and TBHP under standard conditions.



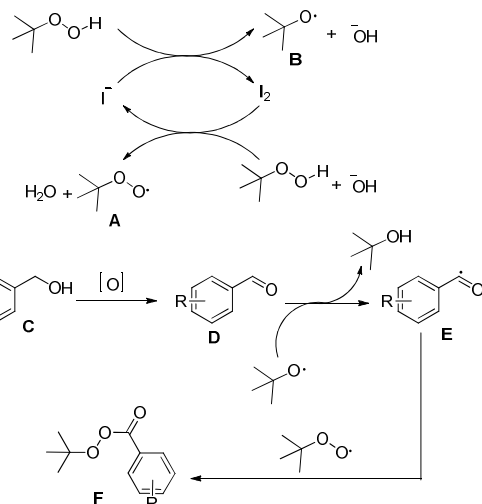
**Scheme 2** A Gram-Scale Preparation of cyclohex-2-en-1-yl 4-chlorobenzoate via Kharasch–Sosnovsky reaction.



**Scheme 3** Investigation of the reaction mechanism.

In order to elucidate the mechanism of this reaction, control experimental was carried out. When radical scavengers like TEMPO was added to the reaction, the yield of the product was decreased dramatically (Scheme 3). This suggested that the transformation probably proceeded through a radical progress.

According to the above results as well as the known literature,<sup>3,5</sup> a plausible reaction mechanism of the reaction which is similar with the catalytic cycle proposed by Wan etc.<sup>3</sup> is proposed in Scheme 4. Firstly, the *tert*-butoxyl **B** and *tert*-butylperoxy **A** radicals were generated from the reaction between TBHP and TBAI. Then aldehyde **D** which is generated the oxidation of alcohol **C** reacted with *tert*-butoxyl **B** to afford the acyl radical **E**. Finally, the desired perester were formed from the reaction between the acyl radical **E** and the *tert*-butylperoxy **A**.



**Scheme 4** Possible reaction pathways.

## Conclusions

In summary, we have discovered a new method for the synthesis of *tert*-butyl peresters catalysed by TBAI directly from commercially available and low-cost acohols and TBHP at room temperature in aqueous system. This method and its combination with Kharasch–Sosnovsky reaction have good potential in synthetic chemistry. Mechanism investigation indicated that a radical process probably included. The further investigation of the reaction mechanism and its applications are underway in our lab.

Financial support from the National Natural Science Foundation of China (21402103), the China Postdoctoral Science Foundation (150030), the Scientific Research Foundation of Shandong Province Outstanding Young Scientist Award (BS2013YY024) and the research fund of Qingdao Agricultural University's High-level Person (631303) were gratefully acknowledged.

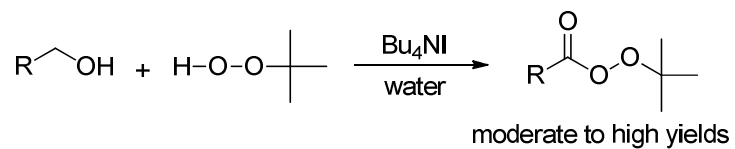
## Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

§  
§§  
etc.

- (a) W. Ando, *Organic Peroxides*, Wiley-Interscience, New York, 1992; (b) S. N. Gupta, I. Gupta and D. C. Neckers, *J. Polym. Sci. Polym. Chem. Ed.* 1981, **19**, 103; (c) L. Wang, X. Liu and Y. Li, *Macromolecules*, 1998, **31**, 3446. (a) P. C. Montevecchi, A. Manetto, M. L. Navacchia and C. Chatgililoglu, *Tetrahedron*. 2004, **60**, 4303; (b) S. Antonello, M. Crisma, F. Formaggio, A. Moretto, F. Taddei, C. Toniolo and F. Maran, *J. Am. Chem. Soc.*, 2002, **124**, 11503; (c) B. K. Shah and D. C. Neckers, *J. Am. Chem. Soc.*, 2004, **126**, 1830. (a) F. Formaggio, M. Crisma, L. Scipionato, S. Antonello, F. Maran and C. Toniolo, *Org. Lett.*, 2004, **6**, 2753; (b) Y. Li, S. Niu, B. Sun, S. Liu, X. Liu and Y. Che, *Org. Lett.*, 2010,

- 12, 3144. (a) D. A. Powell and H. Fan, *J. Org. Chem.*, 2010, **75**, 2726; (b) G. Pelletier and D. A. Powell, *Org. Lett.*, 2006, **8**, 6031. (a) M. S. Kharasch, G. Sosnovsky and N. C. Yang, *J. Am. Chem. Soc.* 1959, **81**, 5819; (b) M. B. Andrus and J. C. Lashley, *Tetrahedron*, 2002, **58**, 845; (c) J. Eames and M. Watkinson, *Angew. Chem. Int. Ed.*, 2001, **40**, 3567; (d) A. V. Malkov, M. Bella, V. Langer and P. Koc, *Org. Lett.*, 2000, **2**, 3047; (e) M. B. Andrus and Z. Zhou, *J. Am. Chem. Soc.*, 2002, **124**, 8806; (f) A. S. Gokhale, A. B. E. Minidis and A. Pfaltz, *Tetrahedron Lett.*, 1995, **36**, 1831; (g) M. T. Rispens, C. Zondercu and B. L. Feringa, *Tetrahedron, Asymmetry*, 1995, **6**, 661; (h) Y. Kohmura and T. Katsuki, *Tetrahedron Lett.*, 2000, **41**, 3941.
- 2 (a) N. Milas and D. M. Surgenor, *J. Am. Chem. Soc.*, 1946, **68**, 642; (b) S. L. Silbert and D. Swern, *J. Am. Chem. Soc.*, 1959, **81**, 2364; (c) N. A. Milas, D. G. Orphanos and R. J. Klein, *J. Org. Chem.*, 1964, **29**, 3099; (d) M. Y. Lu, R. Bao, W. Liu and Y. Li, *J. Org. Chem.*, 1995, **60**, 5341; (e) Y. Hamada, A. Mizuno, T. Ohno and T. Shioiri, *Chem. Pharm. Bull.*, 1984, **32**, 3683.
- 3 W. Wei, C. Zhang, Y. Xu and X. Wan, *Chem. Commun.*, 2011, **47**, 10827.
- 4 (a) M. Kirihara, Y. Asai, S. Ogawa, T. Noguchi, A. Hatano and Y. Hirai, *Synthesis*, 2007, 3286; (b) P. Finkbeiner and B. J. Nachtsheim, *Synthesis*. 2013, 979. (a) M. Uyanik, H. Okamoto, T. Yasui and K. Ishihara, *Science*, 2010, **328**, 1376; (c) T. Froehr, C. P. Sindlinger, U. Kloeckner, P. Finkbeiner, B. J. Nachtsheim, *Org. Lett.*, 2011, **13**, 3754; (d) M. Lamani and K. R. J. Prabhu, *J. Org. Chem.*, 2011, **76**, 9552; (e) Z. J. Liu, J. Zhang, S. Chen, E. Shi, Y. Xu and X. B. Wan, *Angew. Chem. Int. Ed.*, 2012, **51**, 1; (f) L.-T. Li, J. Huang, H.-Y. Li, L.-J. Wen, P. Wang and B. Wang, *Chem. Commun.*, 2012, **48**, 5187; (g) J. Feng, S. Liang, S.-Y. Chen, J. Zhang, S.-S. Fu and X.-Q. Yu, *Adv. Synth. Catal.*, 2012, **354**, 1287; (h) M. Uyanik and K. Ishihara, *ChemCatChem.*, 2012, **4**, 177; (i) J. A. Souto, D. Zian and K. J. Muniz, *Am. Chem. Soc.*, 2012, **134**, 7242; (j) E. Shi, Y. Shao, S. Chen, H. Y. Hu, Z. J. Liu, J. Zhang and X. B. Wan, *Org. Lett.*, 2012, **14**, 2936.
- 5 (a) L. Chen, E. Shi, Z. Liu, S. Chen, W. Wei, H. Li, K. Xu and X. Wan, *Chem. Eur. J.*, 2011, **17**, 4085; (b) B. Tan, N. Toda and C. F. Barbas III, *Angew. Chem. Int. Ed.*, 2012, **51**, 12538.
- 6 (a) C. Zhu and Y. Wei, *ChemSusChem.*, 2011, **4**, 1082; (b) T. Froehr, C. P. Sindlinger, U. Kloeckner, P. Finkbeiner and B. J. Nachtsheim, *Org. Lett.*, 2011, **13**, 3754; (c) L. Ma, X. Wang, W. Yu and B. Han, *Chem. Commun.*, 2011, 11333; (d) U. Kloeckner, N. M. Weckenmann and B. J. Nachtsheim, *Synlett*, 2012, **23**, 97–100; (e) S. Chen, Y. Xu, X. Wan, *Org. Lett.*, 2011, **13**, 6152; (f) J. Xie, H. Jiang, Y. Cheng and C. Zhu, *Chem. Commun.*, 2012, 979; (g) Z. Liu, J. Zhang, S. Chen, E. Shi, Y. Xu and X. Wan, *Angew. Chem. Int. Ed.*, 2012, **51**, 3231; (h) W. Mai, H. Wang, Z. Li, J. Yuan, Y. Xiao, L. Yang, P. Mao and L. Qu, *Chem. Commun.*, 2012, 10117; (i) H. Li, J. Xie, Q. Xue, Y. Cheng and C. Zhu, *Tetrahedron Lett.*, 2012, **53**, 6479. (j) X. Zhang and L. Wang, *Green Chem.*, 2012, **14**, 2141.
- 7 (a) A. Rodriguez and W. J. Moran, *Org. Lett.*, 2011, **13**, 2220;



A new method for the synthesis of *tert*-butyl peresters directly from available alcohols catalyzed by  $\text{Bu}_4\text{NI}$  in aqueous system was developed.