REGULAR ARTICLE



Synthesis of new alkenyl iodobenzoate derivatives *via* Kharasch-Sosnovsky reaction using *tert*-butyl iodo benzoperoxoate and copper (I) iodide

SAADI SAMADI^{*}, AKRAM ASHOURI, SHIVA MAJIDIAN and HERSH I RASHID Laboratory of Asymmetric Synthesis, Department of Chemistry, Faculty of Science, University of Kurdistan, Sanandaj 66177-15175, Iran E-mail: s.samadi@uok.ac.ir

MS received 23 April 2020; revised 22 July 2020; accepted 4 September 2020

Abstract. The synthesis of new alkenyl iodobenzoate derivatives as allylic esters was investigated *via* the reaction of *tert*-butyl iodobenzoperoxoate with alkenes in the presence of copper salts. The best result was obtained using *tert*-butyl-iodobenzoperoxoate in the presence of copper (I) iodide (5 mol%) in refluxing acetonitrile with good yield (92%) in 32 h. The structure of peresters and alkenyl iodobenzoate derivatives were characterized on the basis of their FT-IR, ¹HNMR, ¹³CNMR, and Mass spectra.

Keywords. Kharasch–Sosnovsky reaction; Allylic C–H bond oxidation; *tert*-Butyl iodobenzoperoxoate; Alkenyl iodobenzoate; copper (I) iodide; Alkenes.

1. Introduction

In 1958, Kharasch and Sosnovsky reported the preparation of allylic esters *via* allylic C-H bond oxidation of olefins using *tert*-butyl perbenzoate in the presence of catalytic copper (I) bromide in refluxing benzene.^{1,2} Because of the special nature of the allylic C-H bond, it can be replaced by the benzyloxy group directly.^{1–10} This kind of reaction introduces a suitable synthetic route for preparing the pharmaceuticals and natural products^{11–14} such as leukotriene B₄ as inflammation mediator,¹⁵ chrysanthemic acid,¹⁶ amyrin¹⁷ and brevetoxin.¹⁸ Essentially, the successful development of allylic C–H bond oxidation relies strongly on the copper salt, the perester oxidant, and the reaction conditions such as additives, solvents, and temperature.^{1,3–10}

The literature survey only shows two reports for the synthesis of alkenyliodobenzoate derivatives: In 2000, the Andrus' group reported the synthesis of allylic esters from cyclohexene and cyclopentene for the first time by using *tert*-butyl *o*-iodo benzoperoxoate in the presence of bi-*o*-tolyl bisoxazoline ligands and $Cu(CH_3CN)_4PF_6$ resulted in 68% and 61% yields,

respectively at -20 °C after 120 h in acetonitrile.¹⁹ And in 2005 Branchaud group reported the synthesis and application of cyclohexnyl-2-iodobenzoate as a precursor for Heck reaction.²⁰ However allylic C-H bond oxidation in different conditions generally suffers from long reaction time and moderate yields. Hence, as a part of our ongoing research on Kharasch-Sosnovsky reaction for developing the preparation of allylic esters and the importance of iodo-allylic esters as intermediates in organic synthesis,^{9,19,21–27} we encouraged to synthesis the new derivatives of them through Kharasch and Sosnovsky reaction. Herein, we report the preparation of new iodo-allylic esters from alkenes in the presence of copper salts in good to excellent yields.

2. Experimental

2.1 Synthesis of iodobenzoyl chlorides 2a-c

To a round bottom flask under the nitrogen atmosphere, o-iodo-benzoic acids **1a** (3.0 mmol, 0.74 g) and dried methylene chloride (10 mL) were added. After cooling

^{*}For correspondence

Electronic supplementary material: The online version of this article (https://doi.org/10.1007/s12039-020-01852-8) contains supplementary material, which is available to authorized users.

to 0 °C, oxalyl chloride (6 mmol, 0.62 mL) and dimethylformamide (60 μ L) were slowly added. The mixture was warmed up to room temperature and stirred for 8 h (Scheme 1). After the completion of the reaction, the solvent was removed on a rotary evaporator to provide the *o*-iodo-benzoyl chloride **2a** (0.8 g, quantitative). The total yield for *m*-iodo-benzoyl chloride **2b** and *p*-iodo-benzoyl chloride **2c** were 99%, 99%, respectively.

2.2 Synthesis of tert-butyl iodo benzoperoxoate *3a-c*

To a round bottom flask (100 mL) under the nitrogen atmosphere, o-iodo-benzovl chloride 2a (3.0 mmol, 0.8 g) was dissolved in dried methylene chloride (6 mL). After cooling to - 20 °C, pyridine (3.5 mmol, 0.28 mL) and tertbutyl hydroperoxide (3.5 mmol, 0.24 mL) were slowly added and stirred for 4.5 h at -20 °C (Scheme 1). After consumption of o-iodo-benzoyl chloride, the reaction solution was diluted with CH₂Cl₂ (40 mL) and washed with the saturated NaHCO₃ in the workup. The organic phase was evaporated and the obtained residues were purified by silica gel column chromatography (*n*-hexane: EtOAc; 95:5) to afford the tert-butyl-o-iodo benzoperoxoates 3a (98%) vield). The total vield for tert-butyl-m-iodo benzoperoxoates 3b and tert-butyl-p-iodo benzoperoxoates 3c were 92%. respectively (S3-4 in Supplementary 95%. Information).

2.2a tert-Butyl-2-iodobenzoperoxoate **3a**:¹⁹



Light yellow solid; M.p.: 37-41 °C.; FT-IR (KBr) (v_{max}/cm^{-1}): 2926, 1758, 466.; ¹HNMR (300 MHz, CDCl₃): $\delta_{\rm H}$ (ppm) = 7.97 (1H, d, J = 7.9 Hz, Ar), 7.59 (1H, d, J = 7.7 Hz, Ar), 7.42 (1H, t, J = 7.5 Hz, Ar), 7.20 (1H, t, J = 7.6 Hz, Ar), 1.43 (9H, s, CH₃).; ¹³CNMR (75 MHz, CDCl₃): $\delta_{\rm C}$ (ppm) = 165.2, 141.9, 134.3, 133.0, 130.3, 127.9, 93.3, 84.3, 26.2.; m/z (%): 320 (0.2, M), 248 (58), 194 (5), 122 (100), 74 (75).

2.2b tert-Butyl-3-iodobenzoperoxoate 3b:



Light yellow oil.; FT-IR (KBr) (v_{max}/cm^{-1}) : 2922, 1748, 473.; ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ (ppm) = 8.44 (1H, s, Ar), 8.18 (1H, d, J = 8.1 Hz, Ar), 8.14 (1H, d, J = 8.4 Hz, Ar), 7.64 (1H, m, Ar), 1.45 (9H, s, CH₃).; ¹³C NMR



Scheme 1. The synthesis of alkenyl iodobenzoate derivatives via allylic C-H bond oxidation

(100 MHz, CDCl₃): $\delta_{\rm C}$ (ppm) = 163.9, 142.2, 136.7, 131.5, 130.1, 128.7, 95.0, 86.4, 25.5; m/z (%): 320 (0.26, M), 248 (60), 194 (7), 122 (100), 74 (75).

2.2c tert-Butyl-4-iodobenzoperoxoate 3c:²⁸



Light yellow oil.; FT-IR (KBr) (v_{max}/cm^{-1}): 2933, 1752, 471.; ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ (ppm) = 7.82 (2H, d, J = 8.1 Hz, Ar), 7.78 (2H, d, J = 7.9 Hz, Ar), 1.45 (9H, s, CH₃).; ¹³C NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ (ppm) = 164.4, 139.5, 131.3, 126.8, 99.1, 88.1, 26.0; m/z (%): 320 (0.22, M), 248 (53), 194 (9), 122 (100), 74 (72).

2.3 General procedure for Kharasch-Sosnovsky reaction using tert-butyl iodo benzoperoxoate

To a Schlenk tube under the nitrogen atmosphere, copper (I) iodide (0.05 mmol, 10 mg), phenyl hydrazine (6 μ L) and acetonitrile (3 mL) were added at room temperature. Then alkenes (3 mmol) and *tert*-butyl-o-iodo benzoperoxoates 3a (0.85 mmol, 0.27 g) were slowly added to the light yellow mixture and stirred at room temperature until TLC analysis showed complete consumption of the tert-butyl-o-iodo benzoperoxoates 3a (Scheme 1). After that, acetonitrile was removed under the reduced pressure and the obtained residue was extracted with 10% NH4OH and EtOAc. The organic phase was dried with anhydrous MgSO₄, and then purified by silica gel column chromatography using nhexane and ethyl acetate (90:10) to afford the o-iodo-allylic esters (yield up to 92%). The *m*-iodo-allylic esters and *p*iodo-allylic esters were obtained in a similar procedure (S_{5-} ₂₀ in electronic supplementary material).

2.3a Cyclopent-2-en-1-yl 2-iodobenzoate 4a:¹⁹



Colorless oil, FT-IR (KBr) (v_{max}/cm^{-1}): 3054, 2926, 1718, 1653, 458.; ¹H NMR (300 MHz, CDCl₃): δ_H (ppm) = 7.98 (1H, d, J = 7.9 Hz, Ar), 7.75-7.80 (1H, m, Ar), 7.39 (1H, t, J = 7.2 Hz, Ar), 7.14-7.17 (1H, m, Ar), 6.19-6.21 (1H, m, HC=CH), 5.96-6.00 (2H, m, HC=CH and H-C-O), 2.57-2.60 (1H, m, CH₂), 2.38-2.43 (3H, m, CH₂).; ¹³C NMR (100 MHz, CDCl₃): δ_C (ppm) = 166.7, 141.2, 138.3, 135.7, 132.4, 130.9, 128.9, 127.9, 93.9, 82.1, 31.2, 29.8.; m/z (%): 314 (0.3, M), 248 (9), 127 (27), 111 (38), 97 (65), 85 (100), 57 (78).

2.3b Cyclohex-2-en-1-yl 2-iodobenzoate 5a:^{19,20}



Light yellow oil.; FT-IR (KBr) (v_{max}/cm^{-1}) : 3063, 2932, 1722, 1649, 462.; ¹H NMR (300 MHz, CDCl₃): δ_H (ppm) = 7.99 (1H, d, J = 7.9 Hz, Ar), 7.79 (1H, d, J = 7.6 Hz, Ar), 7.40 (1H, t, J = 7.5 Hz, Ar), 7.12-7.17 (1H, m, Ar), 6.00-6.05 (1H, m, HC=CH), 5.90 (1H, d, J = 1.4 Hz, HC=CH), 5.54 (1H, d, J = 2.8 Hz, H-C-O), 1.95-2.13 (6H, m, CH₂).; ¹³C NMR (100 MHz, CDCl₃): δ_C (ppm) = 166.4, 141.2, 135.7, 133.3, 132.4, 130.9, 127.9, 125.2, 93.9, 69.5, 29.7, 24.9, 18.8.; m/z (%): 328 (0.5, M), 248 (6), 231 (11), 127 (15), 111 (25), 97 (49), 85 (71), 57 (100).





Light yellow oil.; FT-IR (KBr) (v_{max}/cm^{-1}): 3042, 2929, 1758, 1585, 466.; ¹H NMR (400 MHz, CDCl₃): δ_H (ppm) = 8.39 (1H, s, Ar), 8.03 (2H, t, *J* = 7.5 Hz, Ar), 7.53-7.56 (1H, m, Ar), 6.11-6.08 (1H, m, HC=CH), 5.94-5.81(1H, m, HC=CH), 5.63-5.58 (1H, m, H-C-O), 2.01-2.07 (m, 6H, CH₂).; ¹³C NMR (100 MHz, CDCl₃): δ_C (ppm) = 165.3, 141.8, 137.7, 132.2, 131.8, 130.4, 128.5, 127.8, 96.3, 70.2, 30.1, 25.1, 20.0.; m/z (%): 328 (0.5, M), 248 (8), 231 (11), 127 (14), 111 (25), 97 (55), 85 (71), 57 (100).

2.3d Cyclohex-2-en-1-yl 4-iodobenzoate 5c:



Light yellow oil.; FT-IR (KBr) (v_{max}/cm^{-1}): 3042, 2929, 1758, 1585, 466.; ¹H NMR (400 MHz, CDCl₃): δ_H

(ppm) = 7.77-7.84 (4H, m, Ar), 6.03-6.06 (1H, m, HC=CH), 5.85-5.86 (1H, m, HC=CH), 5.52-5.53 (1H, m, H-C-O), 1.85-2.20 (m, 6H, CH₂).; ¹³C NMR (100 MHz, CDCl₃): δ_C (ppm) = 165.8, 137.7, 133.1, 131.1, 130.3, 125.5, 100.5, 69.0, 28.4, 24.9. 18.9.; m/z (%): 328 (0.5, M), 248 (6), 231 (11), 127 (17), 111 (25), 97 (61), 85 (71), 57 (100).

2.3e Cyclooct-2-en-1-yl 2-iodobenzoate 6a:



Red oil.; FT-IR (KBr) (ν_{max}/cm^{-1}): 3072, 2967, 1717, 1644, 475.; ¹H NMR (300 MHz, CDCl₃): δ_H (ppm) = 7.98 (1H, d, J = 7.9 Hz, Ar), 7.78-7.81 (1H, m, Ar), 7.40 (1H, t, J = 7.6 Hz, Ar), 7.12-7.17 (1H, m, Ar), 5.90-5.95 (1H, m, HC=CH), 5.62-5.72 (2H, m, HC=CH and H-C-O), 2.88-2.92 (m, 1H, CH₂), 2.27-2.40 (m, 1H, CH₂), 2.13-2.17 (m, 4H, CH₂), 1.61-1.66 (m, 4H, CH₂).; ¹³C NMR (300 MHz, CDCl₃): δ_C (ppm) = 166.0, 141.2, 135.6, 132.5, 131.1, 130.6, 130.3, 127.9, 94.1, 74.1, 35.1, 28.8, 26.3, 25.8, 23.4.; m/z (%): 356 (0.4, M), 248 (12), 230 (6), 127 (28), 124 (100), 57 (65).

2.3f Cyclooct-2-en-1-yl 2-iodobenzoate 6c:



Light red oil.; FT-IR (KBr) (v_{max}/cm^{-1}): 3077, 2954, 1725, 1675, 456.; ¹H NMR (400 MHz, CDCl₃): δ_H (ppm) = 7.77-7.83 (4H, m, Ar), 5.91-5.93 (1H, m, HC=CH), 5.72-5.79 (1H, m, HC=CH), 5.60-5.64 (1H, m, H-C-O), 2.31-2.40 (2H, m, CH₂), 2.06-2.20 (4H, m, CH₂), 1.46-1.65 (4H, m, CH₂).; ¹³C NMR (100 MHz, CDCl₃): δ_C (ppm) = 165.5, 137.7, 131.1, 130.4, 130.3, 130.1, 100.5, 73.4, 35.1, 28.4, 26.4, 25.9, 23.4.; m/z (%): 356 (0.6, M), 248 (18), 230 (6), 127 (27), 124 (100), 57 (73).

2.3g Cycloocta-2,6-dien-1-yl 2-iodobenzoate 7a:



(ppm) = 7.96 (1H, d, J = 7.3 Hz, Ar), 7.78 (1H, d, J = 6.4 Hz, Ar), 7.36-7.40 (1H, m, Ar), 7.13 (1H, d, J = 6.2 Hz, Ar), 6.23-6.25 (1H, m, HC=CH), 5.62-5.68 (4H, m, HC=CH and H-C-O), 2.83-2.88 (1H, m, CH₂), 2.53-2.60 (3H, m, CH₂), 2.15-2.35 (2H, m, CH₂).; ¹³C NMR (75 MHz, CDCl₃): δ_C (ppm) = 166.0, 141.2, 135.4, 132.6, 130.9, 129.8, 129.6, 129.5, 128.7, 127.9, 125.1, 94.1, 74.0, 33.9, 28.0, 27.9.; m/z (%): 354 (0.7, M), 248 (34), 228 (10), 127 (19), 122 (100), 57 (65), 54 (100).

2.3h Cycloocta-2,6-dien-1-yl 4-iodobenzoate 7c:



Red to brown oil.; FT-IR (KBr) (v_{max}/cm^{-1}): 3072, 2953, 1726, 1668, 472.; ¹H NMR (400 MHz, CDCl₃): δ_H (ppm) = 7.76 7.84 (4H, m, Ar), 6.21-6.23 (1H, m, HC=CH), 5.58-5.75 (4H, m, HC=CH and H-C-O), 2.84-2.88 (1H, m, CH₂), 2.53-2.61 (3H, m, CH₂), 2.26-2.35 (2H, m, CH₂).; ¹³C NMR (100 MHz, CDCl₃): δ_C (ppm) = 165.5, 137.7, 131.1, 130.0, 129.9, 129.4, 128.9, 125.1, 100.7, 73.4, 33.9, 28.0, 27.9.; m/z (%): 354 (0.5, M), 248 (43), 228 (12), 127 (23), 122 (92), 57 (52), 54 (100).

2.3i Cyclohex-2-en-1-yl benzoate 10:



Colorless oil.; FT-IR (KBr, cm⁻¹): 3065, 2939, 1711, 1653, 1491, 1066.; ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ (ppm) = 8.08-8.10 (2H, m, Ar), 7.56-7.60 (1H, m, Ar), 7.45-7.48 (2H, m, Ar), 6.03-6.05 (1H, m, HC=CH), 5.88-5.89 (1H, m, HC=CH), 5.54 (1H, dd, J = 3.4, 1.6 Hz, H-C-O), 1.62-2.16 (6H, m, CH₂).; ¹³C NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ (ppm) = 166.2, 132.9, 132.8, 130.8, 129.6, 128.2, 125.8, 68.6, 28.4, 25.0, 19.0.; m/z (%): 202 (0.5, M), 122 (23), 111 (37), 97 (54), 85 (53), 57 (100).

3. Results and Discussion

3.1 Catalytic allylic C–H bonds oxidation (Kharasch - Sosnovsky reaction)

The synthesis of allylic esters **4-9** performed in moderate to excellent yields from the allylic C-H bond oxidation of alkenes with *tert*-butyl iodo

Red to brown oil.; FT-IR (KBr) (v_{max}/cm^{-1}): 3080, 2959, 1737, 1659, 486.; ¹H NMR (300 MHz, CDCl₃): δ_H

Table 1.



Effect of copper salts, temperature, solvent and the loading of copper (I) iodide on allylic C-H bond oxidation of cyclohexene.

Entry	Cu salts (mol%)	Solvent (3 mL)	Temperature (°C)	Time (h)	Yield (%)
1	$Cu(OAc)_2$ (5)	Acetonitrile	25	135	55
2	$CuSO_4$ (5)	Acetonitrile	25	>160	40
3	$Cu(NO_3)_2$ (5)	Acetonitrile	25	90	55
4	$CuCl_2$ (5)	Acetonitrile	25	82	56
5	CuO (5)	Acetonitrile	25	>180	52
6	$Cu_2O(5)$	Acetonitrile	25	70	60
7	CuCl (5)	Acetonitrile	25	66	66
8	CuBr (5)	Acetonitrile	25	60	70
9	CuI (5)	Acetonitrile	25	50	78
$10^{\rm a}$	CuI (5)	Acetonitrile	25	64	70
11	CuI (5)	Acetonitrile	10	75	62
12	CuI (5)	Acetonitrile	40	42	82
13	CuI (5)	Acetonitrile	50	40	80
14	CuI (5)	Acetonitrile	60	35	86
15	CuI (5)	Acetonitrile	Reflux	32	92
16	CuI (5)	Acetone	Reflux	36	70
17	CuI (5)	Dichloromethane	Reflux	75	64
18	CuI (5)	Chloroform	Reflux	80	55
19	CuI (5)	n-Hexane	Reflux	115	21
20	CuI (5)	Benzene	Reflux	90	28
21	CuI (1)	Acetonitrile	Reflux	50	60
22	CuI (2.5)	Acetonitrile	Reflux	43	70
23	CuI (7.5)	Acetonitrile	Reflux	34	84

Bold values indicate the best result A: Absence of PhNHNH₂

benzoperoxoate **3a-c** in the presence of copper salts.^{9,22–24} In order to prepare the desired peresters, the required acid chlorides **2a-c** was first produced by treating iodo benzoic acids **1a-c** with oxalyl chloride in the presence of a catalytic amount of DMF. Then, by treating of **2a-c** with *tert*-butyl-hydroperoxide in the presence of pyridine in dry dichloromethane at -20 °C, the peresters **3a-c** were obtained (Scheme 1).^{9,22–24}

In continuation, the allylic oxidation conditions were optimized by using cyclohexene as substrate and *tert*-butyl *o*-iodo benzoperoxoate **3a** as an oxidant in the presence of various copper salt, solvents and phenyl hydrazine at different temperature. As outlined in Table 1, in the initial step the effect of several copper salts such as copper (II) sulfate, copper (II) nitrate, copper (II) acetate, copper (II) chloride, copper (I) oxide, copper (I) iodide, copper (I) chloride, copper (I) bromide and copper (I) iodide was investigated. The results represented that when

Cu (I) salts were used, the rate of oxidation of cyclohexene to cyclohex-2-en-1-yl 2-iodobenzoate was faster than Cu (II) salts (Table 1).⁴⁻⁶ It could be due to the oxidation state of Cu (II) salts that are less efficient in the O-O cleavage step of perester during the initial step in the mechanism of the reaction. Based on the results, phenyl hydrazine which acts as reducing agents to regenerate Cu(I) in the catalytic cycle that increased the reaction rate and chemical yields (compared entries 9 with 10, Table 1).^{7,29} The effect of temperature on the reaction was also evaluated and as expected, with raising the temperature, the yield and rate of reaction were increased (entries 10-15). In order to evaluate the effect of solvent on the efficiency of the reaction, some different solvents such as acetonitrile, acetone, dichloromethane, chloroform, benzene and *n*-hexane were used which acetonitrile was selected as the best (entries 15-20, Table 1). Thus, the optimal condition was obtained using cyclohexene and

	Alkene +	Perester Cul (5)	mol%), PhNHNH ₂ (6 μL) N (3 mL), Reflux	Allylic ester	
Entry	Alkene	Perester	Allylic ester	Time (h)	Yield (%)
1	\bigcirc			40	85
2	\bigcirc			32	92
3				42	76
4				37	90
5	\bigcirc			40	85
6	\bigcirc			34	87
7				48	73
8		O O O O O O O O O O O O O O O O O O O		34	90
9	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~			160	<20
10	$\sim\sim\sim\sim$		0 0 9	120	<10

Table 2. Synthesis of allylic esters using perester in the presence of copper (I) iodide and phenyl hydrazine in refluxing acetonitrile

tert-butyl-*o*-iodo-benzoperoxoate **3a** in the presence of copper (I) iodide in refluxing acetonitrile which afforded cyclohex-2-en-1-yl 2-iodobenzoate **5a** with 92% yield during 32 h (entry 15).^{22–24,30} The

investigation of the effect of the loading of copper (I) iodide, was shown that the reaction with 5 mol % of copper (I) iodide offered the best result (compared entries 21-23 with 15, Table 1).^{9,21-24}



Scheme 2. Proposed mechanism for synthesis of cyclohex-2-en-1-yl-2-iodobenzoate 5a and cyclohex-2-en-1-yl benzoate 10.

We extended the obtained optimized condition using other alkenes and peresters. According to the results, cylopentene, cycloheptene and 1,5-cyclooctadiene were also converted to the corresponding allylic esters 4a-7a in good yields and less reaction time (Table 2).^{9,21-24} On the other hand, acyclic olefins such as 1-hexene and 1-octene under optimized condition proceeded with low yields in a long time of reaction (entries 9, 10). By altering the iodide position on peresters (tert-butyl-m-iodo-benzoperoxoate 3b and *tert*-butyl-*p*-iodo-benzoperoxoate **3c**), the allylic esters 5b-c, 6c, 7c were obtained with similar results in comparison 4a-7a. It should be mentioned, under optimized condition the dehalogenated side-product such as cyclohex-2-en-1-yl benzoate (10) was observed in low yield up to 15% (Scheme 2).

3.2 Proposed reaction mechanism

A proposed mechanistic rationalization for allylic C-H bond oxidation of cyclohexene³⁰⁻³⁸ in the presence of copper (I) iodide^{5,22} have been shown in Scheme 2. The cleavage of oxygen-oxygen bond in the *tert*-butyl 2-iodo benzoperoxoate **3a** by copper (I) iodide results in Cu (II) *o*-iodobenzoate **A** and *tert*-butoxy radical. This radical removes hydrogen from allylic position of

cyclohexene to obtain cylohexenyl radical which adds to Cu (II) *o*-iodo benzoate **A** to produce Cu(III) *o*iodobenzoate **B**.^{37–40} The intermediate **B** can rearrange *via* a seven-membered cyclic transition state to produce cyclohex-2-en-1-yl-2-iodobenzoate **5a** copper (I) iodide^{30,37,41,42} (Scheme 2). If *tert*-butoxy radical abstracts the iodide radical from the intermediate **A**, intermediate **C** is produced that removes the allylic hydrogen from cyclohexene and the side product **10a** is afforded throughout pericyclic rearrangement of intermediate **D**.

4. Conclusions

In summary, the catalytic allylic oxidation of alkenes by using *tert*-butyl iodo benzoperoxoate was developed in the presence of copper salts under different conditions and new alkenyl iodobenzoate derivatives were synthesized in moderate to good yields up to 92% within reasonable reaction times. Examination of the generality of this protocol proved the type of alkenes, the size of the cyclic substrate and the position of iodide on perester could affect the yield and the rate of the reaction. Further investigation on asymmetric allylic oxidation and the potential applications of alkenyl iodobenzoate as a precursor for Heck and other Pd-catalyzed reaction is underway in our laboratory.

Supplementary Information (SI)

Supplementary information (including materials and characterization methods, ¹H and ¹³C spectra for synthesized compounds) associated with this article can be found at www.ias.ac.in/chemsci.

Acknowledgements

We are grateful to the University of Kurdistan Research Councils and Iranian National Science Foundation (Proposal No: 95838133) for the partial support of this work.

References

- 1. Kharasch M, Sosnovsky G and Yang N 1959 Reactions of t-butyl peresters. I. The reaction of peresters with olefins1 *J. Am. Chem. Soc.* **81** 5819
- Kharasch M and Sosnovsky G 1958 The reactions of t-butyl perbenzoate and olefins-a stereospecific reaction *J. Am. Chem. Soc.* 80 756
- 3. García-Cabeza A L, Marín-Barrios R, Moreno-Dorado F J, Ortega M J, Massanet G M and Guerra F M 2014 Allylic oxidation of alkenes catalyzed by a copperaluminum mixed oxide *Org. Lett.* **16** 1598
- 4. Shi E, Shao Y, Chen S, Hu H, Liu Z, Zhang J and Wan X 2012 Tetrabutylammonium iodide catalyzed synthesis of allylic ester with tert-butyl hydroperoxide as an oxidant *Org. Lett.* **14** 3384
- 5. Tran B L, Driess M and Hartwig J F 2014 Coppercatalyzed oxidative dehydrogenative carboxylation of unactivated alkanes to allylic esters via alkenes J. Am. Chem. Soc. **136** 17292
- 6. Wang C Y, Song R J, Wei W T, Fan J H and Li J H 2015 Copper-catalyzed oxidative coupling of acids with alkanes involving dehydrogenation: facile access to allylic esters and alkylalkenes *Chem. Commun.* **51** 2361
- Eames J and Watkinson M 2001 Catalytic allylic oxidation of alkenes using an asymmetric Kharasch-Sosnovsky reaction Angew. Chem. Int. Ed. 40 3567
- 8. Rawlinson D J and Sosnovsky G 1972 One-step substitutive acyloxylation at carbon. Part I. Reactions involving peroxides *Synthesis* **1972** 1
- Samadi S, Ashouri A and Ghambarian M 2017 Use of CuO encapsulated in mesoporous silica SBA-15 as a recycled catalyst for allylic C–H bond oxidation of cyclic olefins at room temperature *RSC Adv.* 7 19330
- 10. Andrusc M B and Lashley J C 2002 Copper catalyzed allylic oxidation with peresters *Tetrahedron* **58** 845
- 11. Cuthbertson J D and MacMillan D W 2015 The direct arylation of allylic sp^3 C-H bonds via organic and photoredox catalysis *Nature* **519** 74
- Zhang F L, Hong K, Li T J, Park H and Yu J Q 2016 Functionalization of C (sp³)-H bonds using a transient directing group Science 351 252

- Zheng C and You S L 2014 Recent development of direct asymmetric functionalization of inert C–H bonds *RSC Adv.* 4 6173
- 14. Hartwig J F and Larsen M A 2016 Undirected, homogeneous C–H bond functionalization: challenges and opportunities ACS Cent. Sci. 2 281
- Hayes R and Wallace T W 1990 A simple route to methyl 5S-(benzoyloxy)-6-oxohexanoate, a key intermediate in leukotriene synthesis *Tetrahedron Lett.* 31 3355
- 16. Ficini J and d'Angelo J 1976 Une nouvelle voie d'acces a l'acide (±) chrysanthemique trans *Tetrahedron Lett.* 17 2441
- 17. Alvarez E, Diaz M T, Perez R, Ravelo J L, Regueiro A, Vera J A, Zurita D and Martin J D 1994 Simple designs for the construction of complex trans-fused polyether toxin frameworks A linear strategy based on entropically favored oxirane ring enlargement in epoxycycloalkenes followed by carbon-carbon or carbon-oxygen bondforming cyclizations J. Org. Chem. **59** 2848
- Corey E and Lee J 1993 Enantioselective total synthesis of oleanolic acid, erythrodiol,. beta.-amyrin, and other pentacyclic triterpenes from a common intermediate *J. Am. Chem. Soc.* 115 8873
- Andrus M B and Asgari D 2000 Asymmetric allylic oxidation with biarylbisoxazoline-copper (I) catalysis *Tetrahedron* 56 5775
- Woodcock S R and Branchaud B P 2005 Effect of ether versus ester tethering on Heck cyclizations *Tetrahedron Lett.* 46 7213
- Faraji L, Samadi S, Jadidi K and Notash B 2014 Synthesis of novel chiral diamino alcohols and their application in copper-catalyzed asymmetric allylic oxidation of cycloolefins *Bull. Korean Chem. Soc.* 35 1989
- 22. Samadi S, Jadidi K, Khanmohammadi B and Tavakoli N 2016 Heterogenization of chiral mono oxazoline ligands by grafting onto mesoporous silica MCM-41 and their application in copper-catalyzed asymmetric allylic oxidation of cyclic olefins J. Catal. 340 344
- 23. Samadi S, Jadidi K and Notash B 2013 Chiral bisoxazoline ligands with a biphenyl backbone: development and application in catalytic asymmetric allylic oxidation of cycloolefins *Tetrahedron: Asymm.* **24** 269
- 24. Samadi S, Nazari S, Arvinnezhad H, Jadidi K and Notash B 2013 A significant improvement in enantioselectivity, yield, and reactivity for the copper-bi-o-tolyl bisoxazoline-catalyzed asymmetric allylic oxidation of cyclic olefins using recoverable SBA-15 mesoporous silica material *Tetrahedron* **69** 6679
- 25. Alvarez L X, Christ M L and Sorokin A B 2007 Selective oxidation of alkenes and alkynes catalyzed by copper complexes *Appl. Catal A: Gen.* **325** 303
- 26. Andrus M B and Sekhar B 2001 Synthesis and preliminary use of naphthyl quinazoline and isoquinoline oxazolines for asymmetric allylic oxidation J. *Heterocycl. Chem.* 38 1265
- 27. Andrus M B and Zhou Z 2002 Highly enantioselective copper–bisoxazoline-catalyzed allylic oxidation of cyclic olefins with tert-butyl p-nitroperbenzoate *J. Am. Chem. Soc.* **124** 8806
- 28. Hua J, Guo S, Yang Z, Fang Z and Guo K 2017 Microfluidic Synthesis of tert-Butyl Peresters via KI-

Catalyzed Oxidative Coupling of Methyl Arenes and tert-Butyl Hydroperoxide *Org. Process Res. Dev.* **21** 1633

- 29. Sekar G, DattaGupta A and Singh V K 1998 Asymmetric Kharasch reaction: catalytic enantioselective allylic oxidation of olefins using chiral pyridine bis (diphenyloxazoline)–copper complexes and tert-butyl perbenzoate *J. Org. Chem.* **63** 2961
- Samadi S, Ashouri A, Kamangar S and Pourakbari F 2019 2-Aminopyrazine-functionalized MCM-41 nanoporous silica as a new efficient heterogeneous ligand for Cu-catalyzed allylic C–H bonds oxidation of olefins *Res. Chem. Intermed.* 46 557
- Beckwith A L and Zavitsas A A 1986 Allylic oxidations by peroxy esters catalyzed by copper salts. The potential for stereoselective syntheses J. Am. Chem. Soc. 108 8230
- 32. Kochi J 1962 The mechanism of the copper salt catalysed reactions of peroxides *Tetrahedron* **18** 483
- Kochi J and Subramanian R 1965 Kinetics of electrontransfer oxidation of alkyl radicals by copper (II) complexes J. Am. Chem. Soc. 87 4855
- 34. Kochi J K 1962 Copper salt-catalyzed reaction of butenes with peresters J. Am. Chem. Soc. 84 774
- 35. Kochi J K and Krusic P J 1968 Isomerization and electron spin resonance of allylic radicals *J. Am. Chem. Soc.* **90** 7157

- Mayoral J A, Rodríguez-Rodríguez S and Salvatella L 2008 Theoretical insights into enantioselective catalysis: the mechanism of the Kharasch–Sosnovsky reaction *Chem. Eur. J.* 14 9274
- 37. Walling C and Thaler W 1961 Positive halogen compounds. III. allylic chlorination with t-butyl hypochlorite the stereochemistry of allylic radicals1 *J. Am. Chem. Soc.* **83** 3877
- Walling C and Zavitsas A A 1963 The copper-catalyzed reaction of peresters with hydrocarbons J. Am. Chem. Soc. 85 2084
- Bertz S H, Cope S, Murphy M, Ogle C A and Taylor B J 2007 Rapid injection NMR in mechanistic organocopper chemistry. Preparation of the elusive copper (III) intermediate J. Am. Chem. Soc. 129 7208
- 40. Casitas A and Ribas X 2013 The role of organometallic copper (III) complexes in homogeneous catalysis *Chem. Sci.* **4** 2301
- 41. Sadjadi S, Samadi S and Samadi M 2019 Cu $(CH_3 CN)_4 PF_6$ immobilized on halloysite as efficient heterogeneous catalyst for oxidation of allylic C–H bonds in olefins under mild reaction condition *Res. Chem. Intermed.* **45** 2441
- 42. Samadi S, Jadidi K, Samadi M, Ashouri A and Notash B 2019 Designing chiral amido-oxazolines as new chelating ligands devoted to direct Cu-catalyzed oxidation of allylic C-H bonds in cyclic olefins *Tetrahedron* 75 862