Synlett M. Adib et al. Letter

Metal-Free Oxidative C=C Bond Cleavage of Electron-Deficient Enamines Promoted by *tert*-Butyl Hydroperoxide

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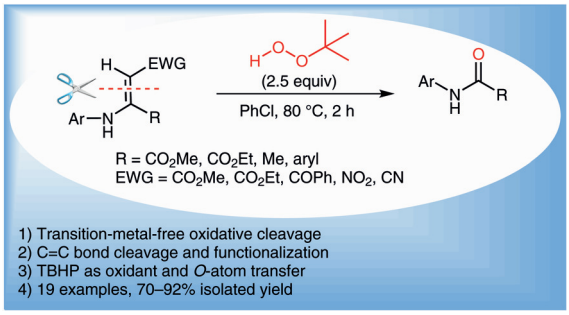

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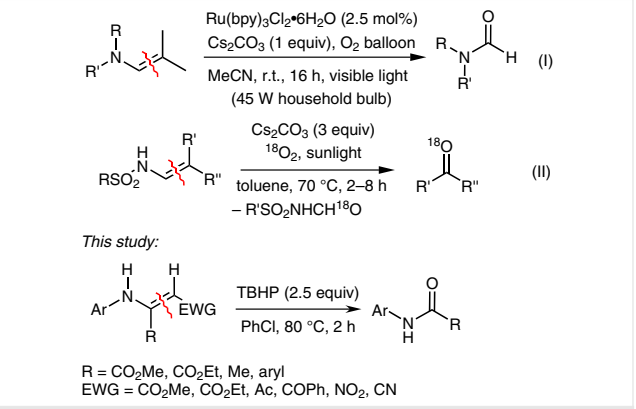
Abstract A novel *tert*-butyl hydroperoxide (TBHP)-promoted oxidative C=C double-bond cleavage of enamines is described. Heating a solution of an electron-deficient enamine in chlorobenzene at 80 °C in the presence of TBHP for two hours led to cleavage of the C=C bond. This study offers a new strategy to carry out C=O double-bond formation by the use of TBHP.

Key words *tert*-butyl hydroperoxide, oxidation, bond cleavage, enamines, oxamates, arylacetamides

Oxidative cleavage of a C=C double bond is capable of providing useful functionalized intermediates, thereby simplifying subsequent chemical transformations.[1] The oxidative cleavage of C–C and C=C bonds in the presence or absence of metals has received significant attention, and catalytic systems based on oxidants such as *tert*-butyl hydroperoxide (TBHP) or oxygen have been widely studied.[2] TBHP is recognized as an attractive reagent in oxidation reactions and also in the formation of various carbon–carbon and carbon–heteroatom bonds, creating molecular complexity that would be unapproachable by other methods.[3,4] Enamines bearing electron-withdrawing substituents are readily accessible, and reactions of these species have received a great deal of attention.[2h,5] Recently, Wang and co-workers reported the photocatalytic cleavage of a series of enamines under visible-light irradiation, leading to the corresponding amides (Scheme 1, eq. I).[6] Additionally, Lee and co-workers developed an oxidative cleavage of the C=C double bond of *N*-sulfonyl enamides in the presence of Cs_2CO_3 in air and on exposure to sunlight (Scheme 1, eq. II).[4e] Wan et al. reported that treating *o*-aminobenzenethiols with enaminones in the presence of CuI and TBHP led to the formation of 2-aroylbenzothiazoles through oxidative C=C bond cleavage.[7]

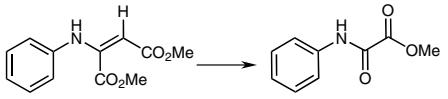
In continuation of our attempts to synthesize biologically active organic compounds[8] and to use oxidants in organic transformations,[9] we describe a unique process for the oxidative C=C bond cleavage of electron-deficient enamines by using TBHP as an oxidant, without the need for metal catalysts, additives, or bases (Scheme 1). In this context, it is worth noting that the use of *N*-aryl enamines in the presence of oxidant systems such as $PhI(OAc)_2$[10] or TBHP/TBAI[11] has led to indole derivatives through an oxidative C–C bond-forming strategy.



Scheme 1 Oxidative C=C bond cleavage of enamines

To evaluate this conversion, we selected dimethyl 2-(phenylamino)maleate (**1a**)[5f] as a model substrate for screening reaction parameters such as the type and amount of oxidant, the solvent, and the reaction temperature (Table 1). Initially, the reaction of **1a** was studied in the presence of TBHP (1 equiv) as an oxidant in chlorobenzene at 25 or

Table 1 Optimization of the Reaction Conditions for the Oxidative C=C Bond Cleavage of **1a** and Conversion into **2a**[a]



1a **2a**

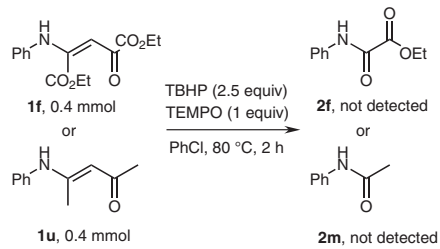
Entry	Oxidant (equiv)	Solvent	Temp (°C)	Yield[b] (%)
1	TBHP[c] (1)	PhCl	25	NR[d]
2	TBHP (1)	PhCl	50	NR
3	TBHP (1)	PhCl	80	45
4	TBHP (1)	PhCl	100	40
5	BPO[e] (1)	PhCl	80	20
6	$K_2S_2O_8$ (1)	PhCl	80	NR
7	H_2O_2[f] (1)	PhCl	80	NR
8	$(NH_4)_2S_2O_8$ (1)	PhCl	80	NR
9	TBHP (2)	PhCl	80	82
10	TBHP (2.5)	PhCl	80	88
11	TBHP (3)	PhCl	80	85
12[g]	TBHP (2.5)	PhCl	80	78
13	TBHP (2.5)	DCE	80	75
14	TBHP (2.5)	MeCN	80	60
15	TBHP (2.5)	toluene	80	50
16	TBHP (2.5)	1,4-dioxane	80	50
17	TBHP (2.5)	DMSO–H_2O (1:1)	80	NR
18	TBHP (2.5)	DMSO	80	NR
19	TBHP (2.5)	H_2O	80	NR
20	–	PhCl	80	NR
21[h]	TBHP (2.5)	PhCl	80	88

[a] Reaction conditions: **1a** (0.4 mmol), solvent (1 mL), 2 h, in air.
[b] Isolated yield.
[c] TBHP = 70 wt% *t*-BuOOH in H_2O.
[d] NR = no reaction.
[e] Benzoyl peroxide.
[f] H_2O_2 = 30 wt% H_2O_2 in H_2O.
[g] Reaction time 3 h.
[h] Under argon.

50 °C, but no product was obtained (Table 1, entries 1 and 2). When the temperature was raised to 80 °C, the corresponding oxamate **2a** was obtained in 45% yield (entry 3). Increasing the temperature to 100 °C led to a lower yield of **2a** (entry 4). The effects of various oxidants were then tested at 80 °C. The yield of oximate **2a** decreased to 20% when BPO was employed (entry 5). Other oxidants such as $K_2S_2O_8$, H_2O_2, and $(NH_4)_2S_2O_8$ had no effect on **1a** (entries 6–8). Therefore, TBHP is the optimal oxidant and 80 °C is the optimal reaction temperature. Next, we examined the effects of varying the amount of TBHP (entries 9–11), and the best result was obtained by using 2.5 equivalents of the oxidant, which gave **2a** in 88% yield (entry 10). When the mixture was heated at 80 °C for more than 2 hours, the yield of **2a** decreased (entry 12). On carrying out the reaction in solvents such as toluene, 1,4-dioxane, DCE, or MeCN with 2.5 equivalents of TBHP, **2a** was obtained in 50–75% yield (entries 13–16). In 1:1 v/v DMSO–H_2O, DMSO, or H_2O, no product was formed (entries 17–19). In the absence of the oxidant, the formation of **2a** did not proceed in chlorobenzene at 80 °C (entry 20). Finally, under an argon atmosphere, the oxidative C=C bond cleavage proceeded efficiently, demonstrating that oxygen has no effect on this process (entry 21). Therefore, the optimal conditions for the transformation of dimethyl 2-(phenylamino)maleate (**1a**) into oxamate **2a** were determined to be TBHP (2.5 equiv) as oxidant in chlorobenzene at 80 °C for 2 hours (entry 10).

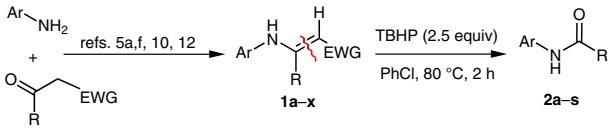
With the optimal conditions in hand, we examined the substrate scope of this method for the formation of a range of alkyl *N*-aryloxamates and *N*-aryl amides. The reaction of dialkyl 2-(arylamino)butene-2-dioates **1a–h**[5a,12] with neutral or electron-donating substituents such as 4-methyl, 2-methoxy, or 4-methoxy or with electron-withdrawing substituents such as 4-chloro or 4-bromo on the aryl ring gave the corresponding alkyl *N*-aryloxamates **2a–h** in good to excellent yields (Table 2, entries 1–8). In addition, the scope of the reaction was extended to ethyl 3-(arylamino)but-2-enoates **1i–r**. Thus, substrates with methyl or aryl groups instead of an ester group in the position α to the nitrogen atom gave the corresponding *N*-aryl amides **2i–r** in 70–80% yield (entries 9–18). In addition, enamines with an acetyl group α to the nitrogen (**1s** and **1t**) gave the *N*-aryl amides **2p** and **2s** in 75% and 76% yield, respectively (entries 19 and 20). Enamines **1u–x** with electron-withdrawing COPh, CN, or NO_2 groups were also successfully employed to give the desired products **2f**, **2i**, and **2j**, respectively, in 73–75% yield (entries 21–24). Unfortunately, enamines **1aa–ad** with an alkylamino group were ineffective in this reaction, and the desired products **2aa–ad** were not detected in their reaction mixtures (entries 25–28).[13]

When the radical scavenger TEMPO was added to the reaction mixture of electron-deficient enamine **1f** or **1u** under the optimized conditions, oxamate **2f** and acetanilide **2m** were not detected, which indicates a radical process is likely to be involved in this reaction (Scheme 2). No adducts containing TEMPO were detected in these reactions.



Scheme 2 Control experiments for the reaction mechanism

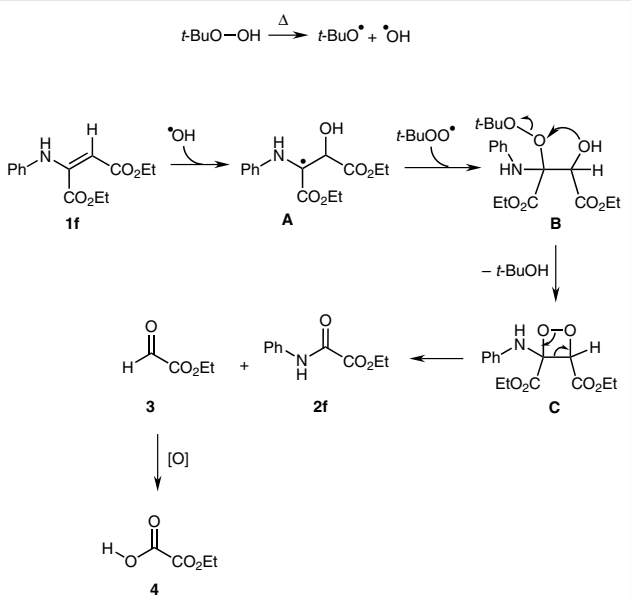
Table 2 Substrate Scope[a]



Entry	Substrate	Ar	R	EWG	Product	Yield[b] (%)
1	**1a**	Ph	CO_2Me	CO_2Me	**2a**	88
2	**1b**	4-MeC_6H_4	CO_2Me	CO_2Me	**2b**	92
3	**1c**	2-$MeOC_6H_4$	CO_2Me	CO_2Me	**2c**	86
4	**1d**	4-$MeOC_6H_4$	CO_2Me	CO_2Me	**2d**	74
5	**1e**	4-BrC_6H_4	CO_2Me	CO_2Me	**2e**	82
6	**1f**	Ph	CO_2Et	CO_2Et	**2f**	85
7	**1g**	4-ClC_6H_4	CO_2Et	CO_2Et	**2g**	80
8	**1h**	4-BrC_6H_4	CO_2Et	CO_2Et	**2h**	80
9	**1i**	Ph	Ph	CO_2Et	**2i**	77
10	**1j**	4-MeC_6H_4	Ph	CO_2Et	**2j**	78
11	**1k**	2-Br-4-MeC_6H_3	Ph	CO_2Et	**2k**	72
12	**1l**	Ph	4-MeC_6H_4	CO_2Et	**2l**	78
13	**1m**	4-MeC_6H_4	4-MeC_6H_4	CO_2Et	**2m**	80
14	**1n**	4-ClC_6H_4	Ph	CO_2Et	**2n**	75
15	**1o**	4-BrC_6H_4	4-MeC_6H_4	CO_2Et	**2o**	77
16	**1p**	Ph	Me	CO_2Et	**2p**	71
17	**1q**	4-MeC_6H_4	Me	CO_2Et	**2q**	73
18	**1r**	3-$O_2NC_6H_4$	Me	CO_2Et	**2r**	70
19	**1s**	Ph	Me	Ac	**2p**	75
20	**1t**	2-Br-4-MeC_6H_3	Me	Ac	**2s**	76
21	**1u**	Ph	CO_2Et	COPh	**2f**	81
22	**1v**	Ph	Ph	CN	**2i**	73
23	**1w**	Ph	Ph	NO_2	**2i**	75
24	**1x**	4-MeC_6H_4	Ph	CN	**2j**	76
25	**1aa**	Pr	CO_2Me	CO_2Me	**2aa**	NR[c]
26	**1ab**	Bu	CO_2Me	CO_2Me	**2ab**	NR
27	**1ac**	$CH_2CH{=}CH_2$	CO_2Me	CO_2Me	**2ac**	NR
28	**1ad**	Bn	CO_2Me	CO_2Me	**2ad**	NR

[a] Reaction conditions: enamine **1** (0.4 mmol), TBHP (2.5 equiv), PhCl (1 mL), 80 °C, under air, 2 h.
[b] Isolated yields.
[c] NR = No reaction.

A plausible mechanism for the formation of ethyl *N*-phenyloxamate (**2f**) is depicted in Scheme 3. Initially, the O–O bond of TBHP is cleaved thermally to generate *tert*-butoxyl and hydroxyl radicals. Subsequently, the hydroxyl radical adds to the double bond of enamine **1f** to produce the *C*-centered β-hydroxy amine radical **A**.[14] Next, radical **A** couples with a *tert*-butylperoxyl radical to form intermediate **B**.[15] The hydroxy group then attacks the adjacent oxygen atom of the *tert*-butylperoxy moiety to give the 1,2-dioxetane **D**,[2b,f,3b,4e,16] which undergoes fragmentation with loss of ethyl oxoacetate (**3**) to afford ethyl *N*-phenyloxamate (**2f**). Ethyl oxoacetate (**3**) is oxidized under the reaction conditions to give 2-ethoxy-2-oxoacetic acid (**4**). GC-MS analysis of the reaction mixture of **1f** revealed presence of 2-ethoxy-2-oxoacetic acid (**4**) as a byproduct, which supports the proposed mechanism (see Figures S1–S3 in the Supporting Information).



Scheme 3 Possible mechanism for the oxidative C=C bond cleavage of **1f** with TBHP

In summary, we have developed an efficient oxidative C=C bond cleavage of electron-deficient enamines promoted by TBHP as oxidant to give the corresponding alkyl *N*-aryloxamates or *N*-aryl amides. High yields of the products, short reaction times, and moderate temperatures, as well as neutral and metal-free conditions, are the salient features of this method.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1588990.

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(13) **Methyl N-phenyloxamate (2a); Typical Procedure**
In a round-bottomed flask, a mixture of dimethyl 2-(phenylamino)maleate (**1a**; 0.094 g, 0.4 mmol), 70% aq TBHP (0.131 g, 1 mmol), and PhCl (1 mL) was heated in an oil bath at 80 °C for 2 h. When the reaction was complete (TLC), the mixture was cooled to r.t. and the reaction was quenched with sat. aq Na_2SO_3 (1 mL). The mixture was extracted with EtOAc, and the organic phase was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography [silica gel, hexane–EtOAc (8:1)] to give a white solid; yield: 0.063 g (88%); mp 111–113 °C. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 3.98 (s, 3 H, OCH_3), 7.20 (t, J = 7.4 Hz, 1 H, CH), 7.38 (t, J = 7.8 Hz, 2 H, 2 × CH), 7.65 (d, J = 8.1 Hz, 2 H, 2 × CH), 8.72–8.95 (br s, 1 H, NH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 53.5 (OCH_3), 119.3 (2 × CH), 125.1 (CH), 128.8 (2 × CH), 135.7 (C), 153.0, 161.0 (2 × C=O).

N-(2-Bromo-4-methylphenyl)acetamide (2s)
White solid; yield: 0.069 g (76%); mp 116–118 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 2.24 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 7.10 (d, J = 8.3 Hz, 1 H, CH), 7.24 (s, 1 H, CH), 7.47–7.53 (br s, 1 H, NH), 8.12 (d, J = 8.3 Hz, 1 H, CH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.7 (CH_3), 25.0 (CH_3), 119.2 (C), 122.1 (CH), 129.2 (CH), 132.6 (CH), 133.3 (C), 135.5 (C) 168.3 (C=O).

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