

Carbenes

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Polyhalides as Efficient and Mild Oxidants for Oxidative Carbene Organocatalysis by Radical Processes

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Abstract: Simple and inexpensive polyhalides (CCl_4 and C_2Cl_6) have been found to be effective and versatile oxidants in removing electrons from Breslow intermediates under *N*-heterocyclic carbene (NHC) catalysis. This oxidative reaction involves multiple single-electron-transfer (SET) processes and several radical intermediates. The α , β , and γ -carbon atoms of aldehydes and enals could be readily functionalized. Given the low cost of the oxidants and the broad applicability of the reactions, this study is expected to greatly enhance the feasibility of oxidative NHC catalysis for large-scale applications. Also this new SET radical process with polyhalides as single-electron oxidants will open a new avenue in the development of NHC-catalyzed radical reactions.

Oxidation is nearly an unavoidable process in chemical synthesis. In the thiamine pyrophosphate (TPP; Vitamin B1) mediated reactions in the biological systems, pyruvate ferredoxin oxidoreductase (PFOR) is believed to enable two single-electron-transfer (SET) processes which oxidize the Breslow intermediate to an acyl azolium intermediate for further transformations.^[1] In synthetic chemistry with *N*-heterocyclic carbenes (NHCs) as organic catalysts, oxidation of NHC/aldehyde-derived Breslow intermediates to the corresponding acyl azoliums has led to development of numerous useful reactions (Figure 1a).^[2] To date, diphenylquinone (**DQ**), pioneered by Studer and co-workers,^[3a,b] has become a most popular oxidant in NHC catalysis.^[3] This quinone oxidant likely behaves as an electron pair acceptor which converts the Breslow intermediate into an acyl azolium intermediate.^[3b] Despite the amazing success, some of the drawbacks in using the **DQ** oxidant include relatively high cost and inconvenience in separating the stoichiometric amount of reduced **DQ** adduct (hydroquinone) from the

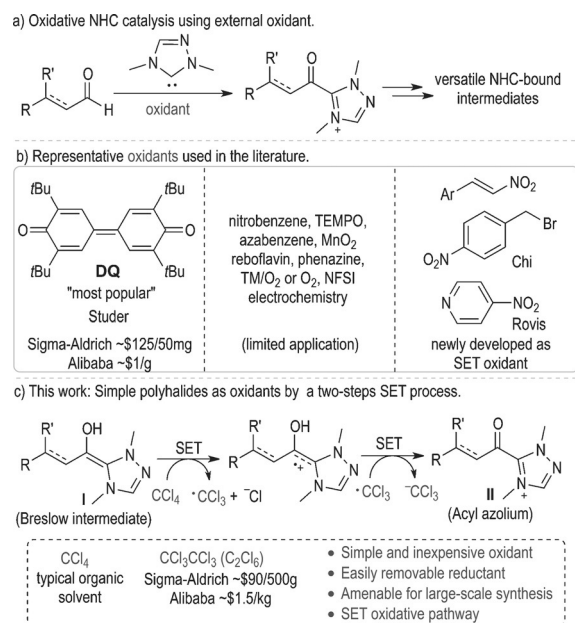


Figure 1. Representative oxidants used in oxidative NHC catalysis and our proposed oxidative pathway using simple polyhalides as oxidants. SET = single-electron transfer.

reaction mixture (Figure 1b). Other common oxidants have also been reported, such as nitrobenzene,^[4] *N*-oxyl radical (e.g., TEMPO),^[5] azabenzene,^[6] MnO_2 ,^[7] riboflavin, phenazine,^[8] a catalytic transition metal (TM) in combination with O_2 as a terminal oxidant^[9] or atmospheric O_2 ,^[10] NFSI,^[11] and electrochemistry.^[12] However, these oxidants are found to have fewer applications because of the various limitations. For example, while O_2 (and air) is in principle an excellent choice as oxidant, its application in NHC catalysis is mostly limited to the conversion of aldehydes into the corresponding carboxylic acids and esters.^[9,10] When O_2 was used as the oxidant for functionalization of the α , β , or γ -carbon of aldehydes, they are unproductively consumed to form simple carboxylic acids or esters as the side products.^[10e]

Our group is interested in the oxidation of Breslow intermediates, through an SET process, for the development of new activation modes and reactions.^[13] In 2013, we reported that α,β -unsaturated nitroalkenes could oxidize aldehydes into the corresponding esters by an SET process.^[13a] Indeed, the nitro groups (NO_2) in several different reagents could behave as SET oxidants in a number of reactions, as independently disclosed by the group of Rovis^[14] and our own group.^[13] Very recently, we found that nitrobenzyl bromide could oxidize aldehydes into esters.^[13c] This

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study encouraged us to evaluate structurally simple and inexpensive polyhalides as oxidants for NHC catalysis.^[15] Herein we report that readily available CCl_4 and C_2Cl_6 can effectively oxidize aldehyde-derived Breslow intermediates to acyl azolium intermediates. In addition to simple carboxylic ester formation, these polyhalides as oxidants allow effective and asymmetric functionalization of the α,β , and γ -carbon atoms of aldehydes and enals. The reactions are very clean as the reduced oxidant (e.g., $\text{CCl}_2=\text{CCl}_2$ from $\text{CCl}_3-\text{CCl}_3$) is essentially a hydroponic volatile solvent which does not require separation. Our oxidation is proposed to go through two SET processes and several radical intermediates (Figure 1c). It provides a practical and inexpensive method amenable for large-scale applications. Additionally, the polyhalo-carbon radicals and NHC-bound radical intermediates generated in our process may find applications in new reaction development.

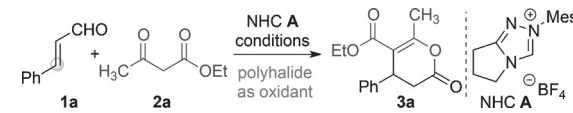
We began our investigation by choosing the formal [3+3] annulation of the enal **1a** and acetoacetate (**2a**) as the model reaction (Table 1).^[16a] We first chose CCl_4 as a potential oxidant owing to its low cost.^[17] To our delight, with the triazolium salt **A**^[18] as an NHC precatalyst, THF as a solvent, and Cs_2CO_3 as a base at 40 °C, the desired [3+3] lactone product (**3a**) was obtained in 41 % yield (entry 1). A switch of CCl_4 to either CHCl_3 , $\text{CH}_2\text{ClCH}_2\text{Cl}$ (DCE), or $\text{CHCl}_2\text{CHCl}_2$ (TCE) as the oxidant did not lead to the formation of **3a** (entry 2). Replacing Cs_2CO_3 with either K_2CO_3 (entry 3) or DABCO (entry 4) as the base gave lower yields of the product. No apparent improvement was observed when other solvents and NHCs were used (entry 5).

The low yields obtained when using CCl_4 as the oxidant was mainly caused by side reactions from CCl_3^- , generated

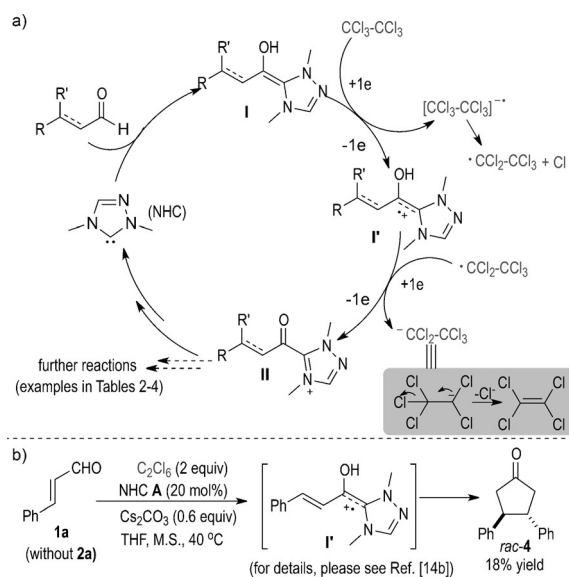
during the redox process. It is known that CCl_3^- and aldehydes can undergo multiple side reactions to give complex mixtures.^[19] We hypothesized that this problem might be solved if the reactive carbanion intermediate could be rapidly quenched. In this regard, hexachloroethane (C_2Cl_6 ; or viewed as $\text{CCl}_3-\text{CCl}_3$) might be a good choice as release of a Cl^- from the pentachloroethyl anion ($^-\text{CCl}_2-\text{CCl}_3$) would furnish tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$), which is inert in the reaction mixture (see Scheme 1a). Fortunately, C_2Cl_6 behaved better than CCl_4 , thus affording **3a** in 61 % yield (Table 1, entry 6). It is worth mentioning that hexachloroethane is a byproduct of many industrial chlorination processes and hence available at very low cost (Figure 1c). Further optimization of the reaction conditions revealed that the reaction proceeded effectively at room temperature by using 1.2 equivalents. C_2Cl_6 as the oxidant (Table 1, entry 7). The reaction yield could be improved from 72 % (entry 7) to 83 % (entry 8) by using a mixture of Cs_2CO_3 and DABCO as the bases. Last, we found that using THF/*t*BuOH (20:1, v/v) as the solvent could provide **3a** with 89 % yield upon isolation (entry 9).

The proposed reaction pathway^[20] is illustrated in Scheme 1a. One electron of the Breslow intermediate **I** (formed between NHC and aldehyde) is removed by the polyhalide (C_2Cl_6) by an SET process to form the radical cation intermediate **I'** and perchloroethane radical anion ($[\text{CCl}_3-\text{CCl}_3]^-$). Release of a Cl^- from radical anion forms a neutral radical intermediate ($^-\text{CCl}_2-\text{CCl}_3$) which could remove one additional electron from the radical cation **I'** to give the unsaturated acyl azolium intermediate **II**. In this process, $^-\text{CCl}_2-\text{CCl}_3$ is reduced to $^-\text{CCl}_2-\text{CCl}_3$, which undergoes the elimination of a Cl^- to form an unreactive $\text{CCl}_2=\text{CCl}_2$. The formation of tetrachloroethylene (TCE) was confirmed by gas chromatography (GC) and ^{13}C NMR analysis (see the Supporting Information). The presence of the NHC-bound enal-derived radical cation intermediate **I'** was evidenced by

Table 1: Screening of polyhalide oxidants for the annulation of **1a** with **2a**.^[a]

				
Entry	Halide (4 equiv)	Base (2 equiv)	T	Yield [%] ^[b]
1	CCl_4	Cs_2CO_3	40	41
2	(HCCl_3 , $\text{CH}_2\text{ClCH}_2\text{Cl}$, or $\text{CHCl}_2\text{CHCl}_2$)	Cs_2CO_3	40	N.R.
3	CCl_4	K_2CO_3	40	30
4	CCl_4	DABCO	40	7
5	(other solvents, NHCs, see SI)			< 46
6	C_2Cl_6	Cs_2CO_3	40	61
7	C_2Cl_6 ^[c]	Cs_2CO_3	RT	72
8	C_2Cl_6 ^[c]	Cs_2CO_3 / DABCO ^[d]	RT	83
9 ^[e]	C_2Cl_6 ^[c]	Cs_2CO_3 / DABCO ^[d]	RT	93 (89) ^[f]

[a] Reaction conditions: The NHC **A** (10 mol %), **1a** (0.05 mmol), **2a** (0.075 mmol), base (2.0 equiv), halide (4.0 equiv), THF (1.0 mL), 4 Å M.S., 12 h. [b] Yield determined by NMR spectroscopy based on **1a** by using 1,3,5-trimethoxybenzene as an internal standard. [c] 1.2 equiv of C_2Cl_6 was used. [d] Cs_2CO_3 (1.2 equiv) and DABCO (1.2 equiv) were used. [e] THF/*t*BuOH (20:1, 1 mL) as the solvent. [f] Yield of isolated product given within parentheses. DABCO = 1,4-diazabicyclo[2.2.2]octane.



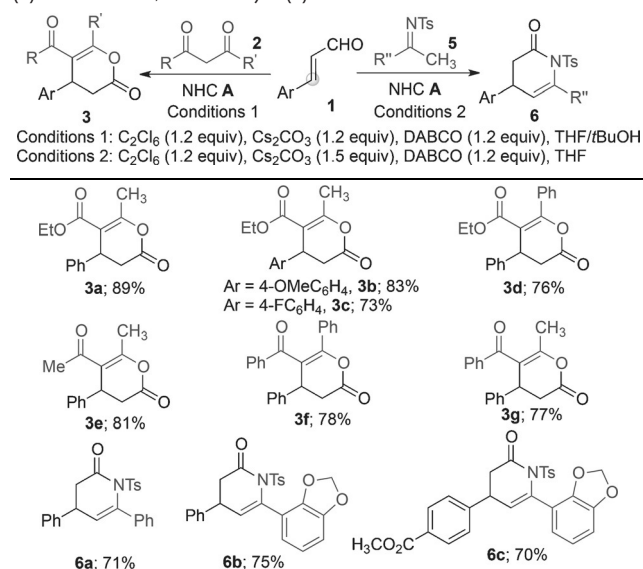
Scheme 1. Proposed reaction pathway (a) and experiment indicating the presence of radical intermediates (b).

the formation of cyclopentanone (**4**), when **1a** was subjected to the reaction conditions in the absence of a nucleophilic substrate (e.g., **2a**; Scheme 1 b). This dimer-forming reaction of an enal through a radical process was reported by Rovis and co-workers.^[14b]

To demonstrate the generality of our oxidation approach using C_2Cl_6 as the oxidant, we studied carbon–carbon bond-forming reactions involving α -, β -, and γ -carbon atoms of aldehydes and enals. In each type of reaction with different substrates, only a slight change of the reaction conditions was necessary (Tables 2, 3, and 4), and clearly indicates the versatile features of the polyhalide oxidants.

Exemplified in Table 2 is the β -carbon reaction of enals under oxidative NHC catalysis. Various enals and 1,3-dicarbonyls reacted effectively to give the lactone products (**3a–g**) with 73–89% yields. The imine **5** (precursor of enamide) could also be used as a nucleophile to react with enals to form lactam products (**6a–c**) in 70–75% yields.^[16b,c]

Table 2: β -Carbon atom reaction:^[a] Examples for the reactions of enals (**1**) with either 1,3-dicarbonyls (**2**)^[b] or imines **5**.^[c]

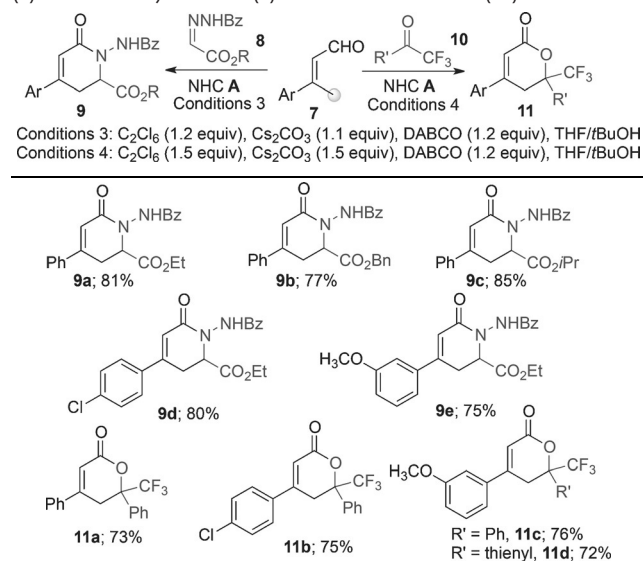


[a] For details, see the Supporting Information. [b] Enal **1** (0.10 mmol, 1.0 equiv), **2** (0.15 mmol), RT for 12 h. Yields of isolated product based on **1**. [c] Enal **1** (0.10 mmol, 1.0 equiv), **5** (0.15 mmol), RT for 12 h. Yields of isolated products based on **1**. Ts = 4-toluenesulfonyl.

We next evaluated our approach for the oxidative γ -carbon atom reaction of enals (Table 3).^[21] Under reaction conditions which were more or less the same as used above for the [3+3] annulations, the γ -carbon atom of the enals (**7**) reacted smoothly with hydrazones (**8**) to provide lactam adducts (**9a–e**) in 75–85% yields.^[21a,b] Activated trifluoromethyl ketones (**10**) could also be used as effective electrophiles in this reaction under similar reaction conditions, thus affording the corresponding unsaturated δ -lactones (**11a–d**) in 72–76% yields.^[21c]

We then studied oxidative α -carbon atom functionalization of aldehydes. The group of Rovis^[8d] and ours^[22a] previously, and independently, employed aliphatic aldehydes

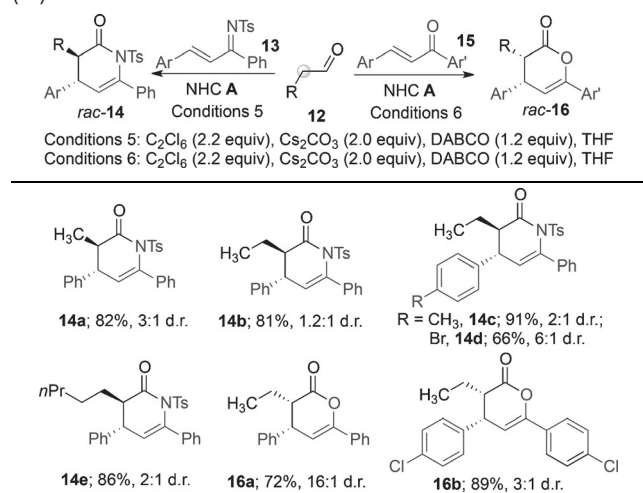
Table 3: γ -Carbon atom reaction:^[a] Examples for the reactions of enals (**7**) with either hydrazones (**8**)^[b] or activated ketones (**10**).^[c]



[a] For details, see the Supporting Information. [b] Enal **7** (0.13 mmol), **8** (0.10 mmol, 1.0 equiv.), RT for 12 h. Yields of the isolated products based on **8**. [c] Enal **7** (0.13 mmol), **10** (0.10 mmol, 1.0 equiv.), RT for 12 h. Yields of the isolated products based on **10**. Bz = benzoyl.

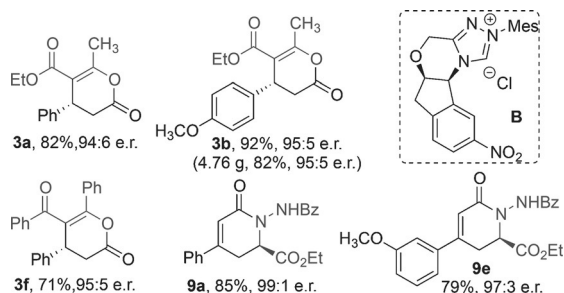
to serve as enolate precursors by oxidative NHC catalysis. Not surprisingly, our method utilizing C_2Cl_6 as the oxidant has the capacity to generate the NHC-bound enolates directly from simple aldehydes. The results in Table 4 illustrate a formal [4+2] cycloaddition of aliphatic aldehydes with α,β -unsaturated imines and ketones to afford six-membered lactams and lactones in good yields.^[22]

Table 4: α -Carbon atom reaction:^[a] Examples for the reactions of aliphatic aldehydes (**11**) with either chalcone imines (**13**)^[b] or enones (**15**).^[c]



[a] For details, see the Supporting Information. [b] Aldehyde **12** (0.22 mmol), **13** (0.10 mmol, 1.0 equiv), RT for 18 h. Yields of combined isolated products based on **13**. [c] **12** (0.30 mmol), **15** (0.10 mmol, 1.0 equiv), RT for 18 h. Yields of combined isolated products based on **15**.

Apparently, our approach with C_2Cl_6 as an oxidant could be directly used in asymmetric catalysis when chiral NHC catalysts are applied (Scheme 2). For example, in the formal [3+3] reactions of enals and 1,3-dicarbonyl compounds, the use of the amino-indanol-derived triazolium NHC catalyst **B**^[23] could lead to the products (**3a,b**, **3f**) with excellent yields and e.r. values. These enantioenriched products could be obtained on a gram scale (4.76 grams **3b**). Similarly, the enal γ -carbon atom functionalized products (e.g., **9a,e**) were also prepared with good yields and excellent e.r. values.



Scheme 2. Asymmetric reactions using polyhalides as oxidants.

In conclusion, polyhalides, such as C_2Cl_6 , can be used as effective oxidants in NHC organic catalysis. This approach allows oxidation of an aldehyde-derived Breslow intermediate into an acyl azolium intermediate. The α -, β -, and γ -carbon atoms of aldehydes and enals could be readily functionalized with our method. On the practical application side, the low cost of the oxidants, the mild reaction conditions, and the simplicity in product purification shall make this method an attractive choice for both small- and large-scale synthesis. On the fundamental side, our oxidation process involves multiple SET processes and radical intermediates, and therefore provides an opportunity for developing new reactions.

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Conflict of interest

The authors declare no conflict of interest.

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