Visible light-assisted ring-opening of cyclic ethers with carboxylic acids mediated by triphenylphosphine and *N*-halosuccinimides

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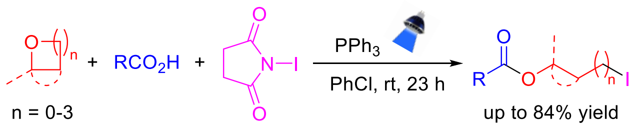
Supporting Information Placeholder



ABSTRACT: The ring-opening of cyclic ethers (epoxide, oxetane, THF, and THP) by carboxylic acids was achieved by using *N*-iodosuccinimide (NIS) or *N*-bromosuccinimide (NBS) and triphenylphosphine under the irradiation of blue light. The corresponding ω-haloalkyl carboxylates were obtained under mild reaction conditions. The reaction is believed to work through a halogen bond complex between NIS (or NBS) and triphenylphosphine, which, upon irradiation with blue light, produces the key phosphine radical cation intermediate that initiates the ring-opening reactions.

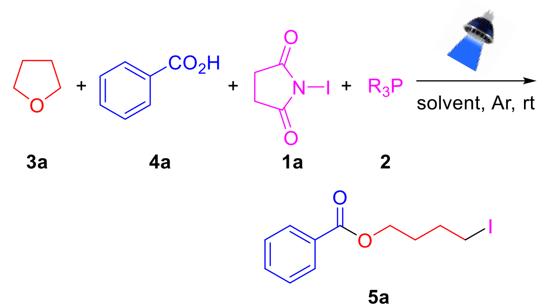
ω-Haloalkyl carboxylates are very useful in organic synthesis because both the halo and the ester groups are highly amenable to synthetic maneuvers.[1] In addition, the ester functional group is ubiquitous in natural products, pharmaceuticals, and biologically active compounds, as well as industrial materials.[2] Ring-opening of cyclic ethers with acid halides, anhydrides, or carboxylates represents the most straightforward method for the synthesis of ω-haloalkyl carboxylates.[3] Alternatively, these compounds can also be obtained by the esterification of ω-haloalcohols with acid chlorides.[4] Nevertheless, most of these method require the use of acid halides, which are not readily available. In addition, a Lewis acid catalyst is also often necessary. There are only a few methods have been reported where the readily available carboxylic acids have been used for the direct synthesis of ω-haloalkyl carboxylates.[1,5] In the regard, Gopinath and Chandrasekaran have developed a one-pot sequential method for the synthesis of ω-bromoalkyl carboxylates via the ring-opening of cyclic ethers involving the acyloxyphosphonium salt intermediates.[5] In 2022, Qiu and coworkers realized the synthesis of ω-iodoalkyl carboxylates directly from carboxylic acids via a Cu-catalyzed ring-opening of cyclic ethers.[1]

Most recently, our group discovered the formation of halogen bond complexes[6,7] between *N*-halosuccinimides and enamines[8a] or polycyclic aromatic hydrocarbons,[8b] which can be used for the direct acyloxylation of ketones or arenes using carboxylic acids under visible light irradiation.[8] While it is well-known that *N*-halosuccinimides form halogen bond complexes with various nitrogen-containing compounds,[7,8] formation of halogen bond complexes between *N*-halosuccinimides and phosphines have not been documented, probably because the combination of *N*-halosuccinimides and phosphines is believed to form only polar reagents.[9] Nevertheless, phosphines and phosphites are known to be good halogen bond acceptors.[10,11] Based on these reports and our own above studies, we hypothesized that *N*-halosuccinimides and phosphines can also form halogen bond complexes and such complexes can be used for realizing novel visible light-assisted chemical reactions. Herein, we wish to report a visible light-assisted direct ring-opening of cyclic ethers using carboxylic acids mediated by the halogen bond complexes, a type of the electron donor-acceptor (EDA) complexes,[12] of triphenylphosphine and *N*-halosuccinimides, via the in-situ-generated phosphine radical cation intermediates.[13]

First of all, we selected *N*-iodosuccinimide (NIS, **1a**) and triphenylphosphine (Ph_3P, **2a**) to test our hypothesis. When NIS (**1a**) or Ph_3P (**2a**) was dissolved in chlorobenzene, only a colorless solution was obtained; however, the 1:1 mixture of **1a** and **2a** in chlorobenzene led to a dark yellow solution. This color change suggests the formation of a halogen bond complex between **1a** and **2a**.[6a] Further evidence supporting the formation of a halogen bond complex between **1a** and **2a** is provided by the UV-vis spectra of these three solutions (see Figure S-1 in the Supporting Information), the UV-vis absorption of the 1:1 Ph_3P/NIS solution is more intense than that of NIS and Ph_3P and shifts to the longer wavelength.[6a]

To find out the potential synthetic utility of this halogen bond complex, the ring-opening of cyclic ethers using carboxylic acids was investigated under visible light irradiation. Using THF (**3a**), benzoic acid (**4a**), NIS (**1a**), and Ph_3P (**2a**) as the model substrates, we first optimized the conditions of the ring-opening reaction. The results are summarized in Table 1. When a slightly excess of

Table 1. Ring-opening of THF mediated by phosphine and NIS[a]



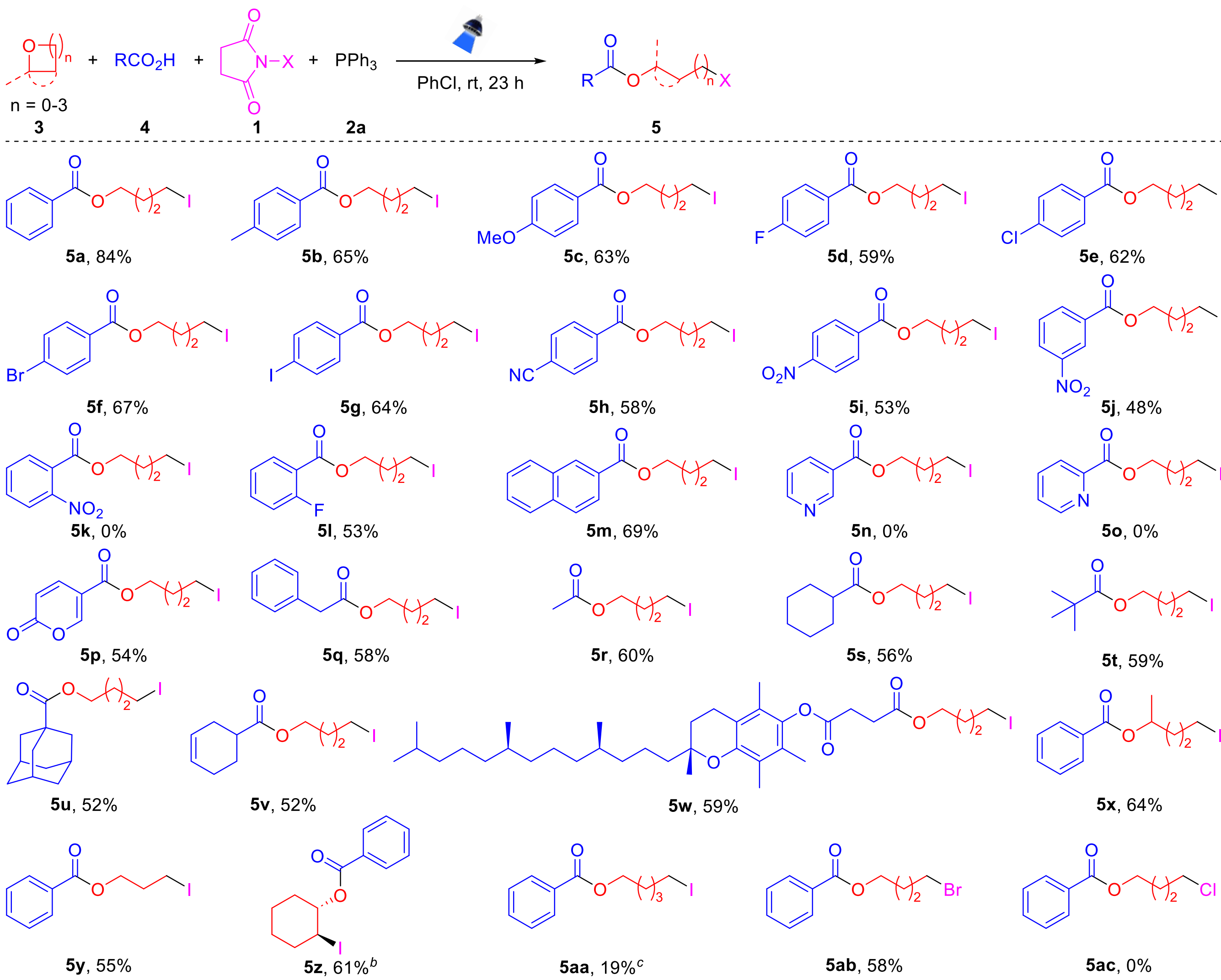
entry	4a (equiv.)	1a (equiv.)	2 (equiv.)	yield of 5a (%)[b]
1	2.0	1.5	Ph_3P (1.5)	84 (95)
2[c]	2.0	1.5	Ph_3P (1.5)	0
3	2.0	1.5	----	0
4[d]	2.0	1.5	Ph_3P (1.5)	48
5	3.0	1.5	Ph_3P (1.5)	43
6	2.0	1.0	Ph_3P (1.0)	10
7	2.0	2.0	Ph_3P (2.0)	48
8[e]	2.0	1.5	Ph_3P (1.5)	23
9[f]	2.0	1.5	Ph_3P (1.5)	13
10[g]	2.0	1.5	Ph_3P (1.5)	48
11[h]	2.0	1.5	Ph_3P (1.5)	24
12[i]	2.0	1.5	Ph_3P (1.5)	44
13[j]	2.0	1.5	Ph_3P (1.5)	15
14[k]	2.0	1.5	Ph_3P (1.5)	0
15[l]	2.0	1.5	Ph_3P (1.5)	0
16[m]	2.0	1.5	Ph_3P (1.5)	48
17	2.0	1.5	$(4\text{-}FC_6H_4)_3P$ (1.5)	(33)
18	2.0	1.5	$(4\text{-}MeOC_6H_4)_3P$ (1.5)	(26)
19	2.0	1.5	$(2\text{-}MeC_6H_4)_3P$ (1.5)	(11)
20	2.0	1.5	$(1\text{-}Nap)_3P$ (1.5)	(27)
21	2.0	1.5	$c\text{-}C_6H_{11}Ph_2P$ (1.5)	(21)
22	2.0	1.5	$(c\text{-}C_6H_{11})_2PhP$ (1.5)	(23)
23	2.0	1.5	$(c\text{-}C_6H_{11})_3P$ (1.5)	(9)

[a]Unless otherwise indicated, all reactions were carried out with THF (**3a**, 1.0 mmol), benzoic acid (**4a**, 2.0 mmol), NIS (**1a**, 1.5 mmol), phosphine **2** (1.5 mmol) in PhCl (5.0 mL) under argon at rt under the irradiation of two 36 W blue LED (460 nm) for 23 h. [b]Yield of the isolated product **5a** after column chromatography. The number in the parentheses represents the conversion of **3a** as determined by the ^1H NMR of the crude reaction product. [c]Carried out in the dark. [d]Carried out under air. [e]Carried out in toluene. [f]Carried out in $CHCl_3$. [g]Carried out in EtOAc. [h]Carried out in acetone. [i]Carried out in CH_3CN. [j]Carried out using THF (**3a**) as the solvent. [k]Carried out in DMF. [l]Carried out in MeOH. [m]Carried out at 50 °C.

4a (2.0 equiv.), **1a** (1.5 equiv.), and **2a** (1.5 equiv.) was employed, an excellent conversion (95%) of **3a** was achieved after the mixture was irradiated in chlorobenzene with blue light at rt for 23 h. The desired ring-opened product **5a** was isolated in 84% yield (entry 1). In contrast, control reactions conducted in the dark (entry 2) or without Ph_3P (entry 3) gave no product. These results clearly evince that both light and Ph_3P are crucial for this reaction. When the same reaction was carried out under air, a much lower yield of **5a** (48%, entry 4) was obtained. Similarly, lower yields of the product were obtained when the loadings of benzoic acid (**4a**), NIS (**1a**), or Ph_3P (**2a**) were adjusted (entries 5-7). When the reaction was conducted in other common organic solvents, such as toluene, $CHCl_3$, EtOAc, acetone, CH_3CN, and THF, the yield of **5a** dropped substantially (entries 8-13). DMF and MeOH are especially bad solvents for this reaction and no formation of **5a** was observed in these two solvents (entries 14-15). Raising the reaction temperature to 50 °C turned out also to be counterproductive for this reaction and the yield of **5a** dropped to 48% (entry 16). Since phosphine is essential for this reaction, we screened several aryl- and alkyl-substituted phosphine derivatives together with NIS in this reaction (entries 17-23). As the results in Table 1 show, none of the other phosphines we screened are as effective as triphenylphosphine (**2a**) in converting THF (**3a**) to the ring-opened product. In summary, these optimizations identified that parameters listed in entry 1 is the best for this ring-opening reaction.

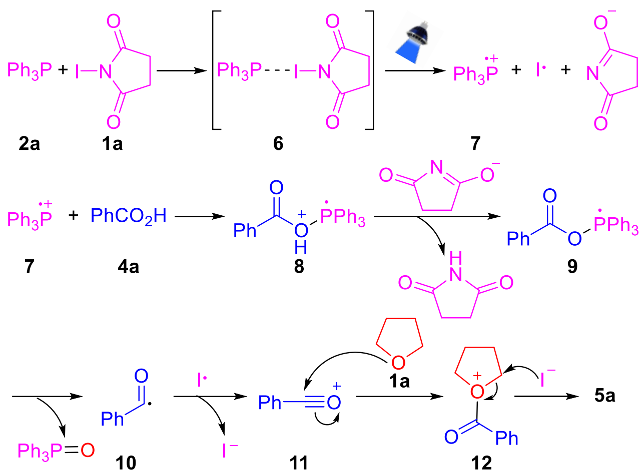
The substrate scope of this reaction was then evaluated. As the results summarized in Table 2 show, besides benzoic acid (**4a**), substituted benzoic acids can also be applied in the THF ring-opening reaction. While in general slight lower yields of the desired ring-opened products (**5b**-**i**) were obtained from the substituted benzoic acids, there is almost no effect on the product yield whether an electron-donating group (such as Me, and MeO, **5b** and **5c**) or an electron-withdrawing group (such as F, Cl, Br, I, CN, or NO_2, **5d**-**i**) is attached to the *para*-position of the phenyl ring. While *meta*-nitrobenzoic acid only led to a slightly lower yield of the desired product (**5j** vs. **5i**), no formation of the desired **5k** was observed for *ortho*-nitrobenzoic acid. This is most likely due to steric effects. Indeed, when 2-fluorobenzoic acid was used in the reaction, the expected product **5l** was obtained 53% yield, which is similar to that of 4-fluorobenzoic acid (**5d**). The desired ring-opened product **5m** of 2-naphthoic acid was also obtained in 69% yield. When heterocyclic acids were applied in this reaction, the outcome of this reaction depends on the actual acid was employed. For examples, while no desired products of picolinic and nicotinic acids (**5n** and **5o**) were obtained, that of coumalic acid (**5p**) was obtained in 54% yield. The failure in the former acids was most likely due to its nitrogen atom, which is known to form halogen bond complex with NIS[7b] and, therefore, interferes the desired halogen bond formation between Ph_3P and NIS. In addition to aryl carboxylic acids, aliphatic carboxylic acids can also be applied in this reaction, and similar yields were obtained for the ring-opened products of 2-phenylacetic acid (**5q**), acetic acid (**5r**), cyclohexanecarboxylic acid (**5s**), pivalic acid (**5t**), and 1-adamantane carboxylic acid (**5u**), which have either a primary, secondary, or tertiary alkyl group attached to the carboxylic acid function group. 3-Cyclohexen-1-carboxylic acid can also be used as a substrate in this ring-opening reaction, and desired **5v** was obtained in 52% yield. The double bond in the acid is tolerated in the reaction. Similarly, the ring-opened product of α-tocopheryl acid succinate (**5w**) was obtained in 59% yield, and its oxygen-containing heterocycle does not affect the reaction. In addition to THF, we also applied some other cyclic ethers in this ring-opening reaction together with benzoic acid. As the results in Table 1 show, when 2-methyltetrahydofuran (**3b**) was employed as the substrate, the ring-opening reaction generated product **5x** in 64% yield, with benzoic acid regioselectively attacking the methyl-substituted side of the THF ring. When oxetane (**3c**) was applied, the expected product **5y** was obtained in 55% yield. Cyclohexene oxide (**3d**), which is an epoxide, can also be used as a substrate in this reaction and the desired product (**5z**) was obtained in 61% as a single *trans*-diastereomer. In contrast, the ring-opening reaction of tetrahydropyran (THP, **3e**) turned out to be more challenging and no product was obtained when the reaction was carried out under the optimized conditions. Nevertheless, when the reaction was carried out at 60 °C, the desired ring-opened product **5aa** could be obtained in a low yield. Finally, we also applied *N*-bromo- (NBS, **1b**) and *N*-chlorosuccinimide (NCS, **1c**) as the halogen bond donors in this reaction. It was found that, while NBS (**1b**) led to the formation of the desired ω-bromoalkylester **5ab** in 58% yield, no formation of the expected ω-chloroalkylester **5ac** was observed from the reaction of NCS (**1c**). These results are not totally unexpected, as NBS and especially NCS are weaker halogen bond donors than NIS.

Table 2. Substrate scope of the ring-opening reactions mediated by triphenylphosphine/*N*-halosuccinimides[a]



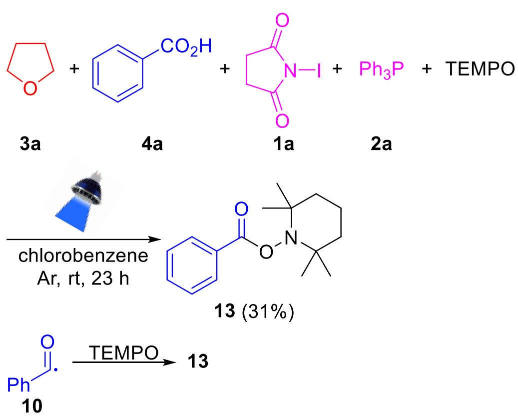
[a]All reactions were carried out with cyclic ether (**3**, 1.0 mmol), carboxylic acid (**4**, 2.0 mmol), NIS (**1a**, 1.5 mmol), triphenylphosphine (**2a**, 1.5 mmol) in PhCl (5.0 mL) under argon at rt under the irradiation of two 36 W blue LED (460 nm) for 23 h. [b]Only the *trans*-diastereomer was obtained. [c]The reaction was carried out at 60 °C.

The formation of iodine was observed in this ring-opening reaction, which was confirmed by the starch test. This observation suggests that iodine radical is produced during the reaction. In addition, we did not observe the formation of any decarboxylation products from the carboxylic acids, including those with a benzyl or tertiary substituent, such as 2-phenylacetic acid, pivalic acid, and 1-adamantane carboxylic acid, suggesting that carbonyloxy radical is not likely involved in this reaction. Based on the results of the experiment using ^{18}O-labeled benzoic acid as the starting material, the C-O σ bond of benzoic acid is broken during this reaction.[13] Thus, the following mechanism is proposed for the ring-opening reaction (Scheme 1). When NIS (**1a**) and Ph_3P (**2a**) are mixed in chlorobenzene, the halogen bond complex **6** forms. Upon the irradiation of the blue light, the electron transfer between the halogen bond acceptor (**2a**) and donor (**1a**) leads to the formation of the triphenylphosphine radical cation (**7**),[14] iodine radical, and the succinimide anion. The reaction of **7** with benzoic acid (**4a**) gives the radical cation intermediate **8**, which yields the phosphoranyl radical[15] **9** after deprotonation. Subsequent elimination of triphenylphosphine oxide from **9** produces the benzoyl radical **10**,[16] which then reacts with iodine radical to give the acylium ion **11** (or benzoyl iodide). Reaction between **11** (or benzoyl iodide) and THF (**3a**) gives intermediate **12**, which is ring-opened by iodide to give **5a**. It should be pointed out that we obtained product **5w** as a single regioisomer when 2-methyltetrahydrofuran was applied as the substrate, which is much higher than that of the in-situ generated benzoyl iodide.[3a] At present, we lack a good explanation for this discrepancy.



Scheme 1. Proposed mechanism for the ring-opening reaction.

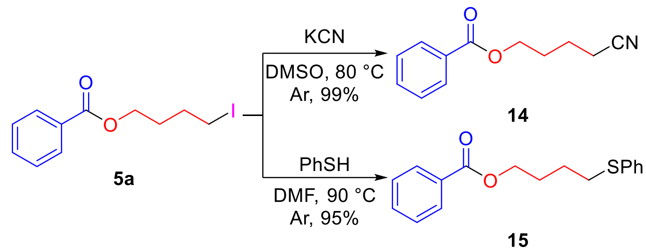
Further support of this triphenylphosphine radical cation-mediated ring-opening mechanism came from the results of a TEMPO inhibition experiment. As shown in Scheme 2 (top equation), the desired product **5a** was not formed when the reaction was carried out in the presence of TEMPO. Instead, we obtained compound **13** in a low yield. Formation of this compound can be the result of the reaction of benzoyl radical (**10**) and TEMPO (Scheme 2, bottom equation).



Scheme 2. TEMPO inhibition experiments.

Qiu and co-workers have demonstrated multiple synthetic applications of ω-iodoalkyl carboxylates.[1] We also conducted some further elaborations of the reaction product **5a** (Scheme 3).

In summary, we demonstrated that formation of a halogen bond complex between *N*-halosuccinimides and triphenylphosphine is possible and the corresponding complexes can be used for the visible light-assisted synthesis of ω-iodoalkyl carboxylates via the direct ring-opening of cyclic ethers by carboxylic acids under very mild conditions.



Scheme 3. Derivatizations of the reaction product **5a**.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information

Supporting Information

The Supporting Information is available free of charge at.

Detailed experimental procedures, compound characterization data, and copy of ^{1}H and ^{13}C NMR spectra of the obtained products (PDF)

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Notes

The authors declare no competing financial interest.

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