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Metal-free Photochemical Atom Transfer Radical Addition (ATRA) of $BrCCl_3$ to Alkenes

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Dedicated to Prof. Ioannis Gallos on the occasion of his retirement

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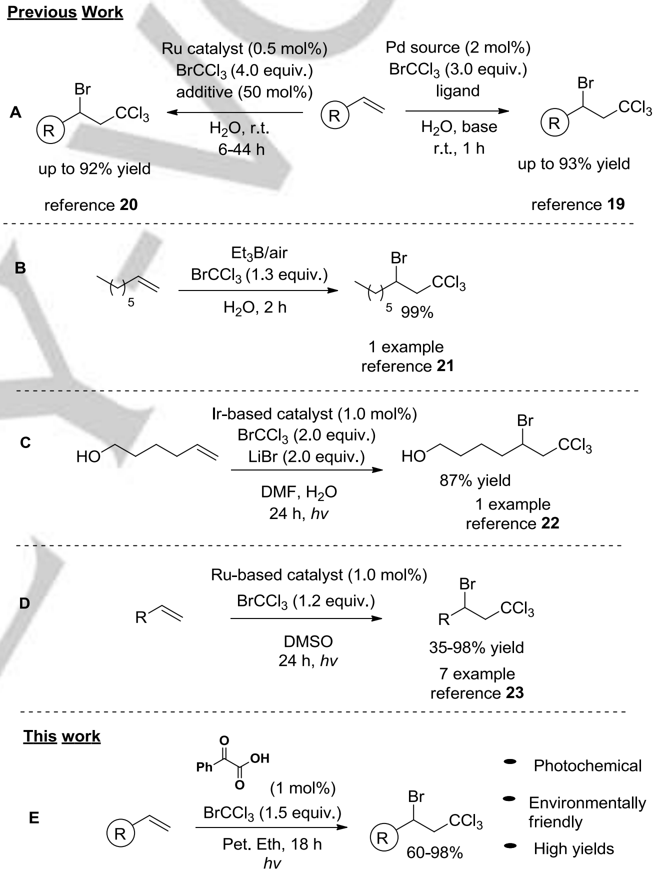
Abstract: A simple, photochemical and metal-free protocol for the atom transfer radical addition (ATRA) of bromotrichloromethane onto various alkenes is described. Among a range of organic molecules, phenylglyoxylic acid proved to be the most suitable photoinitiator to promote a sustainable process for the addition of bromotrichloromethane to olefins. This photochemical atom transfer radical protocol can be expanded into a wide substrate scope of aliphatic olefins bearing various functional groups, leading to the corresponding products in good to excellent yields.

Introduction

Photon has been for many years considered as a “traceless reagent”.[1] Thus, there is a continuous interest into harnessing the power of light in the field of organic synthesis. Therefore, the field of photochemistry, the use of light to promote organic transformations, has received great attention by organic chemists. The transformation of organic molecules utilizing the power of light has become a powerful approach for the activation of organic molecules and chemical bonds, enabling chemical transformations that would otherwise be inaccessible.[2] Ciamician was the first to perform organic reactions using light.[3] Though, the true power of photochemistry was highlighted by the establishment of photoredox catalysis by Macmillan,[4] Yoon[5] and Stephenson,[6] where it was proven the ability of photoredox catalysts to introduce novel organic transformations. As a result, in the following years, more chemists took advantage of photocatalysis for the construction of complex molecules.[7]

The addition of bromoalkanes to alkenes is a very useful reaction, as one can achieve in one reaction, the augmentation of the carbon atom chain and the addition of moieties that can be further functionalized with relative ease. In 1945, Kharasch reported that halocarbons, such as CCl_4, could be added to olefins through an atom transfer radical addition (ATRA) process.[8] A series of examples of ATRA reactions employing haloalkanes have been reported in literature, most of which are metal-catalyzed processes, employing ruthenium,[9] iron,[10] nickel,[11] palladium,[12] iridium[13] and copper[14] based catalysts. Photochemistry has also contributed in the development of ATRA reactions, either employing metal-based photocatalysts[15] or organic molecules.[16,17] Melchiorre, through his seminal work, has developed ATRA reactions into a useful tool in organic chemistry for various radical transformations, employing anisaldehyde as the photocatalyst.[18]



Scheme 1. Synthetic methodologies for ATRA reactions with bromotrichloromethane.

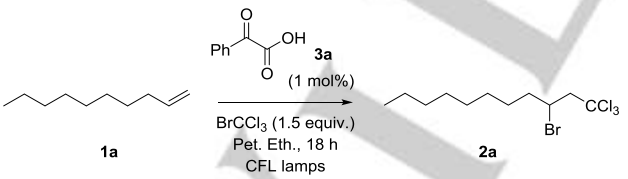
More specifically, regarding the ATRA reaction between bromotrichloromethane and alkenes, in 2002, Oshima developed a method for the atom transfer radical addition of bromotrichloromethane onto olefins using a palladium complex as the catalyst (Scheme 1, **A**).[19] In 2008, Majoral reported the radical addition of bromotrichloromethane to terminal alkenes using a ruthenium-based catalyst (Scheme 1, **A**).[20] In both cases, the use of additives and the high excess of bromotrichloromethane were required for the reaction to proceed. Finally, in 2001, Oshima reported a method, in which triethylborane/O_2 was used as the initiator system in water to provide the corresponding products in good yields.[21] Only one example using bromotrichloromethane was demonstrated, and the reaction was stoichiometric (Scheme 1, **B**). Later, Stephenson presented an iridium-based photochemical protocol for the radical addition of haloalkanes onto olefins (Scheme 1, **C**).[22] However, only one example using bromotrichloromethane was presented and the use of an additive was required. Later, he expanded the scope with a ruthenium-based catalyst.[14a] Along the same lines, our group developed a photocatalytic method, where custom-made ruthenium complexes could be employed as the photocatalyst (Scheme 1, **D**).[23] In 2015, a visible-light mediated transformation, without the use of a photocatalyst, was reported by Zeitler. In that case, blue LEDs were required to be used as the light source and only one example was presented and the reaction was possible in the presence of two equivalents of $BrCCl_3$.[24]

Unfortunately, metal-based complexes can be expensive, and some are not commercially-available. In order to solve this problem, a number of organic dyes have been employed as photocatalysts, which in many cases provide similar reactivities to metal catalysts.[25] Photoorganocatalysis, the use of small organic molecules as catalysts, is a low-cost and environmentally friendly alternative.[26,27] We have recently developed a photochemical protocol that is easy to operate, employing cheap household lamps as the irradiation source and a cheap, organic, and commercially available molecule as the catalyst.[28] Herein, we report a simple and versatile method for the mild and green addition of bromotrichloromethane to alkenes, using phenylglyoxylic acid as the promoter under photochemical conditions (Scheme 1, **E**). The present transformation functionalizes a diverse array of olefins and generates the corresponding haloalkanes in high yields, using low catalyst loading.

Results and Discussion

Our previous photochemical studies hinted that phenylglyoxylic acid could be an excellent initiator for the atom transfer radical addition (ATRA) of bromotrichloromethane to alkenes. Having in mind the work of Zeitler[24] and in an effort to study the influence of the wavelength of the irradiation source in the outcome of the photochemical reaction between bromotrichloromethane and 1-decene (**1a**), we examined various wavelengths of LEDs or CFL household lamps as the light source (Table 1). We studied the reaction in the presence and in the absence of phenylglyoxylic acid (**3a**) in various wavelengths. More specifically, under the irradiation of compact fluorescence lamps (CFL), the presence of the phenylglyoxylic acid facilitated the formation of the product, providing a quantitative yield, while in the absence of **3a** the reaction turned out to be sluggish (Table 1, entry 1). On the other hand, under the use of LEDs, the differences between the reaction yields, in the presence versus the absence of phenylglyoxylic acid, are trivial (Table 1, entries 2-7). Also, it is apparent that increasing the wavelength of the LED, the yield of the reaction drops (Table 1, entries 3-5), until we reach 456 and 525 nm LEDs, where the product is not even detected. The yield differences between our study and literature[24] could be accounted in various factors, such as the reagent stoichiometry, the different solvent and substrate, as well as the difference of the power and source of the LED lamp.

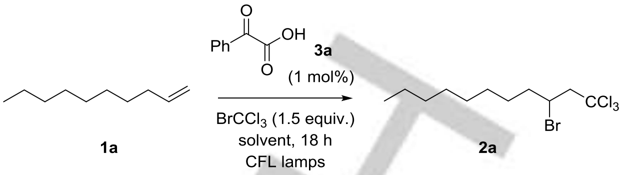
Table 1. Optimization of the light source for the photochemical atom transfer radical addition of bromotrichloromethane to **1a**.



Entry	Wavelength	Yield (%) with **3a**[a]	Yield (%) in the absence of **3a**[a]
1	CFL	100	6
2	370	82	79
3	390	66	66
4	427	64	59
5	440	34	60
6	456	nd	nd
7	525	nd	nd

[a] Yield determined by ^{1}H-NMR using internal standard, nd: not detected. CFL lamps: 2 x 85 Watts, LED lamps: Kessil PR 160L 40 Watts.

Table 2. Optimization of the reaction conditions for the photochemical atom transfer radical addition of bromotrichloromethane to **1a**.

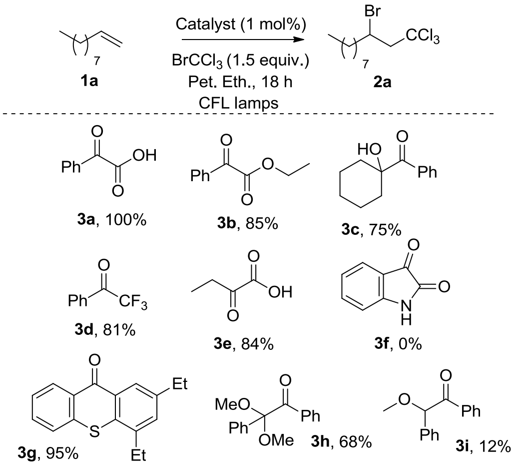


Entry	Solvent	Yield (%)[a]
1	Pet. Eth.	98
2	$CHCl_3$	86
3	Benzene	72
4	THF	75
5	DMSO	0
6	*t*-Amyl alcohol	83
7	MeCN	90
8[b]	Pet. Eth.	96
9[c]	Pet. Eth.	0
10[d]	Pet. Eth.	6

[a] Yield of isolated product, after column chromatography. [b] 1.2 equiv. of $BrCCl_3$ was employed. [c] The reaction was performed in the dark. [d] The reaction was performed without the use of PhCOCOOH. CFL lamps: 2 x 85 Watts.

Next, we turned our attention into optimizing the reaction conditions, employing phenylglyoxylic acid as the photochemical promoter (Table 2). Initially, a range of organic solvents was tested; however, in all cases, the expected product **2a** was obtained in a lower yield (Table 2, entries 2-7). After identifying petroleum ether as the appropriate solvent for the reaction, we further proceeded with the optimization of the reaction conditions (Table 2, entries 8-10).[29] In an attempt to lower the amount of bromotrichloromethane, we employed almost stoichiometric amounts, which led to slightly lower yield (Table 2, entry 8). When the reaction was kept in the dark, 1-decene was not converted into the corresponding product (Table 2, entry 9). Finally, as stated before, in the absence of the phenylglyoxylic acid, **2a** was afforded in very low yield (Table 2, entry 10).

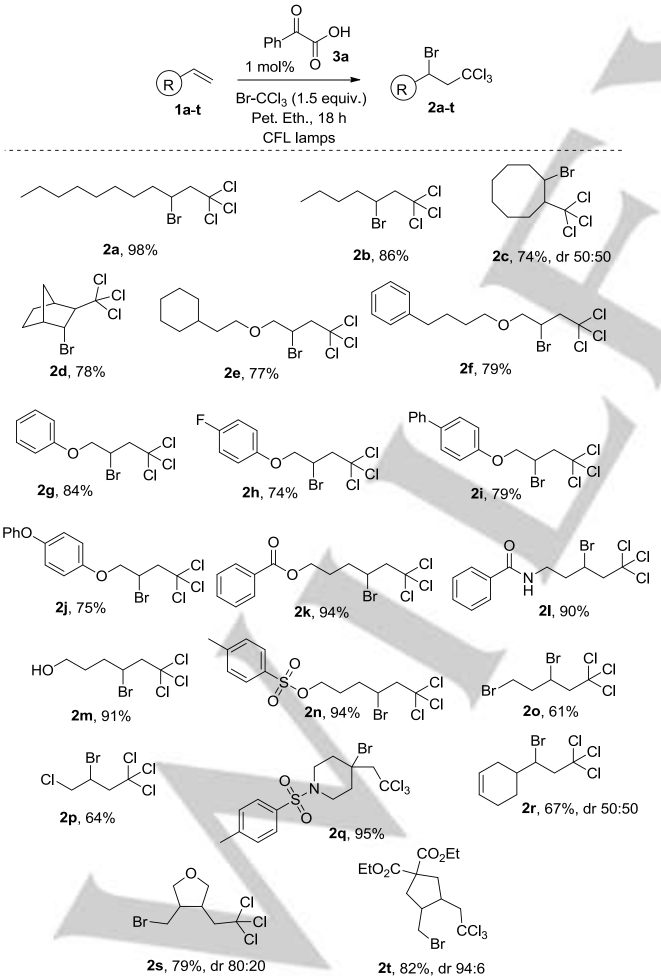
Then, the photochemical radical addition of bromotrichloromethane to 1-decene (**1a**) was examined to identify the appropriate photoinitiator (Scheme 2). A variety of known photoinitiators (**3a-i**) led to moderate to excellent yields.



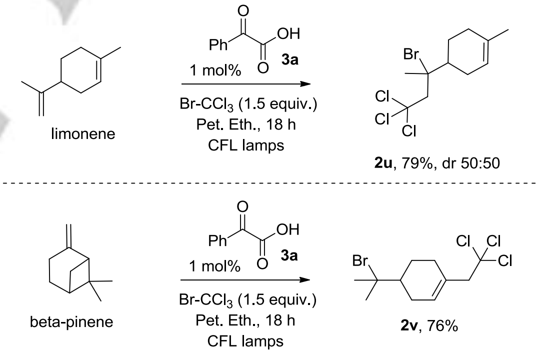
Scheme 2. Initiator screening for the photochemical reaction between bromotrichloromethane and 1-decene. Yield determined by ^{1}H-NMR.

In all cases, a very low catalyst loading of 1 mol% was employed, leading to excellent yields. Phenylglyoxylic acid (**3a**) proved to be the ideal promoter, providing **2a** in quantitative yield.

Our following step was the exploration of the substrate scope of the photochemical ATRA reaction of bromotrichloromethane with various olefins (Scheme 3). All tested substrates were converted into the corresponding products in good to excellent yields. Initially, the atom transfer radical addition was performed with aliphatic olefins, leading to the corresponding products in excellent yields (**2a** and **2b**). Internal cyclic alkenes, which are less reactive for ATRA reactions, including cyclooctene and 2-norbornene, were good substrates, leading to the desired products in high yields (**2c** and **2d**). The class of allyl ethers proved to be a very efficient class of substrates, since the products were obtained in high yields (**2e**-**2j**). Moreover, terminal olefins bearing a wide array of functionalities were efficiently transformed into the corresponding products in good to high yields (**2k**-**2n**). Furthermore, short-aliphatic chain containing halides, like allyl chloride and 4-bromo-1-butene, reacted well, since the corresponding products were obtained in good yields (**2o** and **2p**). 1,1-Disubstituted alkenes reacted also well, leading to **2q** in excellent yield. Vinylcyclohexene, bearing two double bonds, performed the reaction successfully (**2r**), verifying the presence of a long-lived radical intermediate. Interestingly, only the terminal double bond reacted in the reaction conditions. Diallyl ether was also successfully employed leading to cyclic product **2s**.Cyclization was possible not only with oxygen-based molecules, but also with carbon-containing molecules (product **2t**). Finally, naturally-occurring substrates were employed (Scheme 4). When limonene was employed as the substrate, the radical addition occurred only in the less substituted double bond, leading to product **2u**, in a 50:50 mixture of diastereomers. β-Pinene reacted well, leading to the corresponding ring-opened product **2v** in high yield.



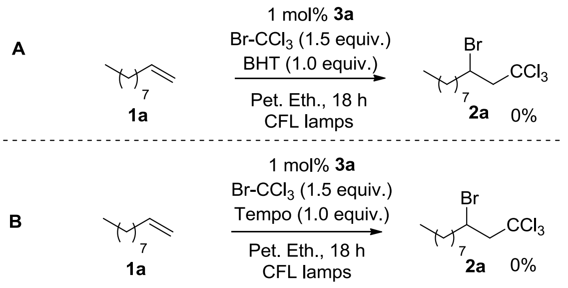
Scheme 3. Substrate scope of the photochemical ATRA of bromotrichloromethane to alkenes.



Scheme 4. Limonene and β-pinene as substrates.

In an effort to shed some light in the reaction mechanism, UV-Vis experiments were performed. The association of an electron-rich molecule with an electron acceptor can lead to the formation of an aggregate, called electron donor-acceptor (EDA) complex. EDA complexes are known in literature, since the 1950s,[30,31] but only recently Melchiorre and others have identified them as active species in photochemical reactions. An EDA complex sometimes is recognized, when upon addition of the two components, an increase in the UV absorbance of the mixture is observed.[31] However, our studies proved that there is no EDA formation in this case.[29]

In a recent report, Yoon employed the quantum yield measurement as a mechanistic tool.[32] A closed photocatalytic system lacks chain propagation and exhibits a maximum theoretical quantum yield of Φ = 1. The chain processes can potentially provide multiple equivalents of product from each



Scheme 5. Mechanistic studies for the photochemical ATRA of bromotrichloromethane to alkenes.

photon absorbed, therefore the quantum yield of a chain reaction is Φ >> 1. Using potassium ferrioxalate as the actinometer,[32,33] we calculated the quantum yield of the reaction (Φ = 11), indicating a chain propagation mechanism.[29] Further optimization and mechanistic studies proved that the reaction has the characteristics of a radical process, since addition of BHT or TEMPO prevents the reaction from occurring (Scheme 5, **A** and **B**).[29]

Next, we studied the photochemical reaction by NMR spectroscopy.[29] Previous studies in our group proposes that the excited triplet state of phenylglyoxylic acid decomposes to different products upon irradiation in different solvents.[28] The process was monitored by ^{13}C- and ^{1}H-NMR spectroscopy and our observations state that excited phenylglyoxylic acid, in petroleum ether, photodecomposes mainly to benzaldehyde.[29] The products of the photodecomposition are observed both in the spectra from the irradiation of phenylglyoxylic alone and of the reaction mixture.[29] According to literature precedents[28] and our own observations,[29] this means that excited $PhCOCO_2H$ is decomposing to benzoyl radical, which is responsible for the initiation of the process. Furthermore, in the absence of either the catalyst or light, the reaction does not proceed. Finally, on-off experiments were carried out and proved that constant irradiation is necessary for the reaction to proceed (Figure 1).[29]
Based on the above experiments, a proposed reaction mechanism is depicted in Scheme 6. Phenylglyoxylic acid upon irradiation, is excited to its singlet and triplet state which can then lead to its decomposition to benzoyl radical (**I**).[28,29] In the presence of bromotrichloromethane, the benzoyl radical (**I**) can abstract the bromine atom furnishing benzoyl bromide (**II**) and trichloromethyl radical (**III**) via a halogen atom transfer (XAT).[34] The latter radical can then react with an electron-rich double bond leading to radical (**IV**), which reacts with another molecule of bromotrichloromethane, leading to product **2a** and trichloromethyl radical (**III**), which takes part in a radical propagation chain process, which is supported by the quantum yield calculated [Φ > 1].[29] Thus, the role of phenylglyoxylic acid is merely that of an initiator.

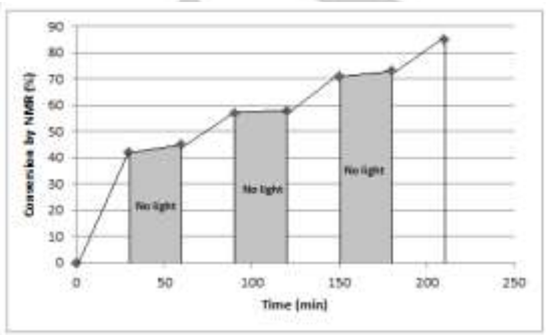
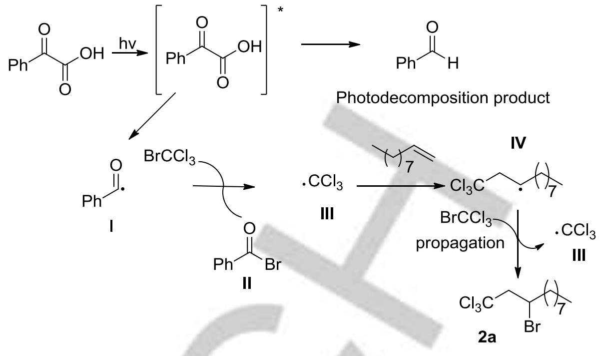


Figure 1. On-off experiments for the photochemical reaction between pentanal and 1-decene.



Scheme 6. Proposed reaction mechanism.

Conclusions

In conclusion, we have developed a green, metal-free and efficient method for the radical addition of bromotrichloromethane to olefins. Various sources of irradiation, CFL lamps and LED lamps of various wavelengths, were tested both in the presence and absence of phenylglyoxylic acid. In CFL lamps, the presence of PhCOCOOH is crucial for product formation, while in LED lamps the yields were comparable. After optimization, the optimum reaction conditions were found and applied in a variety of olefins. Mechanistic studies revealed that phenylglyoxylic acid can be employed in a very low catalyst loading (1 mol%) for the introduction of a low-cost, simple, photochemical protocol for the synthesis of a wide variety of bromo-compounds in excellent yields.

Experimental Section

Green Photochemical Atom Transfer Radical Addition (ATRA) of $BrCCl_3$ to Olefins

In a glass vial with a screw cap containing phenylglyoxylic acid (1.5 mg, 0.01 mmol, 0.01 equiv.) in Petroleum Ether (2 mL), alkene (1.00 mmol, 1.00 equiv.) and $BrCCl_3$ (296 mg, 1.50 mmol, 1.50 equiv.) were added consecutively. The vial was sealed with a screw cap and left stirring under household bulb irradiation (2 x 85 Watts) for 18 h. The desired product was isolated after purification by column chromatography.

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Keywords: Photochemistry · Green Chemistry · ATRA · Olefins · Bromotrichloromethane

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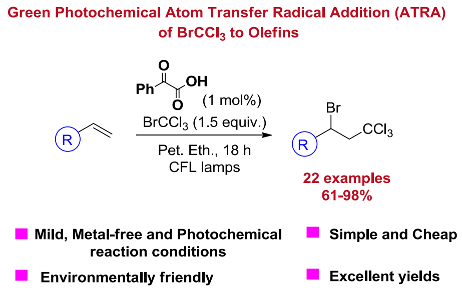
Photochemistry



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Metal-free Photochemical Atom Transfer Radical Addition (ATRA) of $BrCCl_3$ to Alkenes

Photochemistry. Phenylglyoxylic acid can be employed in a very low catalyst loading (1 mol%) for the introduction of a low-cost, simple, photochemical protocol for the ATRA reaction of $BrCCl_3$ with olefins.

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