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Metal-Free and Light-Promoted Radical Iodotrifluoromethylation of Alkenes with Togni Reagent as Source of CF_3 and Iodine

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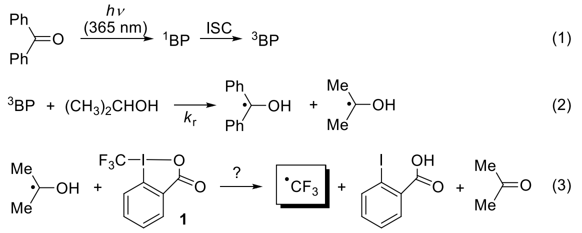
A light-promoted methodology for the iodotrifluoromethylation of alkenes was developped. For the first time the Togni reagent was exploited as the source of both the CF_3 group and iodine atom. Preliminary mechanistic studies suggest that both CF_3I and 2-iodobenzoic acid are direct sources of the iodine atom that is transferred to the products.

The benziodoxolone **1** developed by Togni,[1] the prototype of an ever expanding class of hypervalent iodine reagents,[2] has proved to be a particularly powerful electrophilic trifluoromethylating agent for a variety of chemical functions.[3] While Togni reagent **1** can react directly with nucleophiles,[4] its activation often requires a Bronsted acid,[5] or a transition metal complex acting as a Lewis acid, or as a reducing species to generate the reactive CF_3 radical.[6] Interestingly, a few transition metal free methodologies exploiting the reducing power of radicals or organic reagents to generate the CF_3 radical from **1** have been developed.[7] We now report a light-promoted and transition metal-free methodology for the iodotrifluoromethylation of alkenes which exploits, for the first time, the Togni reagent **1** as the source of both the CF_3 group and iodine atom.

Direct iodotrifluoromethylation of alkenes are particularly interesting reactions as the generated iodo- compounds can subsequently undergo a variety of chemical transformations. Trifluoroiodomethane CF_3I, a powerful reagent for nucleophilic or radical trifluoromethylations,[8] has emerged as a benchmark reagent to conduct the title reaction. Following pioneering work of Hazzeldine on photochemically-initiated radical additions of CF_3I onto alkenes,[9] a few methodologies with limited substrate scope, exploiting $Ru_3(CO)_{12}$ as catalyst,[10] Et_3B,[11] or Me_3Al as stœchiometric reactants,[12] were described. More recently, visible-light photoredox catalysis has emerged as a promising strategy to perform such reaction, either by using CF_3I,[13a-c] or by combining the Umemoto reagent with CsI.[13d] With the objective of developing CF_3I surrogates, Liu and co-workers described an effective procedure to conduct iodototrifluoromethylations on both alkenes and alkynes by combining CF_3SO_2Na and I_2O_5 as a single electron oxidant.[14] These reactions require a high temperature (110 °C), 2 to 3 equiv. of the reactants and rather long reaction times (12 to 27 h). Sodeoka and co-workers reported recently that iodoftrifluoromethylations of alkenes could be conducted very effectively by reacting the alkene with **1** (1.5 equiv.) and KI (1.1 equiv.) under thermal activation (60°C, 1,4-dioxane, 9 h).[15] During this study, while attempting to prepare bromotrifluoromethylated adducts using an ethanolic solution containing KBr, they were surprised to find that the iodotrifluoromethylated product was formed in 38% yield along with 14% of the hydrotrifluoromethylated product. This result was not exploited further, and further studies were not conducted in order to help explain such unusual and intriguing reactivity.

In the course of our studies aiming to develop BP-sensitized (BP = benzophenone) light-promoted alkene and alkyne perfluoroalkylations,[16] we hypothesized that the α-hydroxyisopropyl radical, which is generated with a photochemical quantum yield close to unity by fast reaction (k_r = 1.28 x 10^6 $M^{-1}.s^{-1}$) of the BP triplet state (^3BP) with isopropanol (eq 1-2),[17] could be used as effective reducer of **1** to generate the trifluoromethyl radical (eq 3).



Half-wave oxidation potentials for the α-hydroxyisopropyl radical of –0.61 V and –1.05 V (vs SCE) were measured in

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† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: Experimental procedures, synthesis and characterization of products **2a-p**, **3** and **4**. See DOI: 10.1039/x0xx00000x

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CH_3CN,[18] and H_2O (pH = 7),[19] respectively. Note that the ketyl radical (eq 2) is less reducing, having a redox potential of –0.25 V (vs SCE) in CH_3CN.[18] Moreover, as isopropanol is an excellent H-atom donor we envisioned that the intermediate radical formed by fast addition of the CF_3 radical onto the alkene could rapidly react with *i*-PrOH to afford the hydrotrifluoromethylated products.

When a preliminary reaction was conducted by simply reacting a degassed heterogeneous mixture of the 1-dodecene, **1** (2 equiv.), BP (2 mol%) in *i*-PrOH at room temperature and irradiating the reaction mixture at 365 nm using a low pressure Hg lamp (6W, type TLC = thin layer chromatography),[20] a fast consumption of the alkene and **1** occurred yielding predominantly two trifluoromethylated alkanes in a ~ 6:1 ratio (The ^{19}F NMR spectrum of a typical reaction mixture is given in the SI). Surprisingly, analysis revealed that the major product which was formed in satisfactory (59%) yield was the iodotrifluoromethyl alkane **2a**, while the minor product (12% NMR yield) was the hydrotrifluoromethyl alkane **3**. A series of control experiments (see table S1 in the SI) confirmed that *i*-PrOH and light were mandatory to obtain optimal yields, and that the presence of BP led to an increase of reaction rates by a factor of ~ 5.

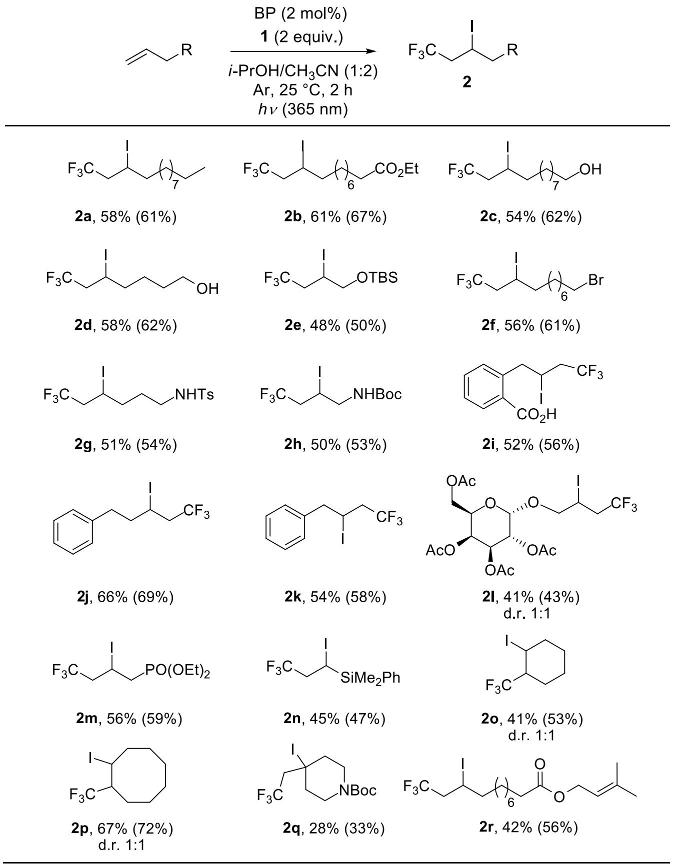
Using the optimized reaction conditions a range of iodotrifluoromethyl alkane compounds **2** could be prepared from various alkenes in 2 h of reaction, the methodology tolerating a variety of functional groups including esters, alcohols, siloxyethers, alkyl bromides, carbamates, carboxylic acids, aromatic rings, phosphonates, and silanes (table 1). The procedure can equally be applied to internal and 1,1-disubstituted alkenes, even if for the latter a modest yield was obtained due to the competitive formation of both trifluoromethylated allylic (19%, ^{19}F NMR yield) and hydrotrifluoromethylated (18%, ^{19}F NMR yield) piperidines. Interestingly, when a substrate containing both a terminal and a trisubstituted alkene was reacted, the trifluoromethylation was shown to occur exclusively on the terminal one.

These results show that even though the reaction yields are only moderate to good, such an operationally simple metal-free iodotrifluoromethylation methodology should be of synthetic utility. In some cases, however, idodotrifluoromethylation failed. For example, no reactivity was observed with styrene. This is most probably due to a very efficient BP triplet state quenching by styrene which occurs with a rate constant (k_q) of 3.3 × 10^9 M^{-1} s^{-1}.[21] Also, when reacting electron-deficient alkenes i.e. the phenyl vinyl sulfone and diethyl vinylphosphonate, the hydrotrifluoromethylated products **4** and **5** were formed almost exclusively and were isolated in ~ 50% yield (scheme 1).

Additional experiments, whose results are given in table 2, have been conducted in order to get insights into such unusual reactivity for the Togni reagent **1**. In the proposed mechanism (scheme 2), α-hydroxyisopropyl radicals are first generated in the initiation step (eq. 1 and 2) by typical BP photoreactivity, i.e. by fast reaction of BP triplet state with *i*-PrOH. The isopropyl alcohol radical could then reduce **1** to generate the CF_3 radical, 2-iodobenzoic acid and acetone.

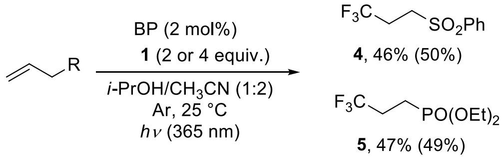
To test this first step of the radical mechanism, the Togni reagent alone was submitted to the optimized reaction conditions and the product yields determined by ^1H and ^{19}F NMR (entry 1 of table 2). After 15 min irradiation, **1** was fully decomposed affording acetone, 2-iodobenzoic acid and iodobenzoic acid in ~ 100%, 80% and 24% yields, respectively.

Table 1. Iodotrifluoromethylation of alkenes using Togni reagent **1**.[a]



2a, 58% (61%)
2b, 61% (67%)
2c, 54% (62%)
2d, 58% (62%)
2e, 48% (50%)
2f, 56% (61%)
2g, 51% (54%)
2h, 50% (53%)
2i, 52% (56%)
2j, 66% (69%)
2k, 54% (58%)
2l, 41% (43%) d.r. 1:1
2m, 56% (59%)
2n, 45% (47%)
2o, 41% (53%) d.r. 1:1
2p, 67% (72%) d.r. 1:1
2q, 28% (33%)
2r, 42% (56%)

[a] Conditions: Reactions conducted at 25°C for 2 h (4 h for **2r**) under irradiation at 365 nm (TLC lamp) on 0.5 mmol scale with **1** (1 mmol), BP (2 mol%) in *i*-PrOH (1.7 mL)/CH_3CN (3.3 mL) and degassing by Ar bubbling (20 min); Isolated yields with ^{19}F NMR yields given in parenthesis; Diastereomeric ratios determined by ^{19}F NMR on the crude reaction mixture.



Scheme 1. Hydrotrifluoromethylation of alkenes using Togni reagent **1** (Isolated yields with ^{19}F NMR yields given in parenthesis).

Only two fluorinated products were detected by ^{19}F NMR, i.e. CF_3H generated in ~ 68% yield and CF_3I which, to our surprise was formed in up ~ 23% yield (The ^{19}F NMR spectrum is given in the SI). These results strongly support a first step in which CF_3 radicals are very effectively and rapidly generated by reduction of **1** by the α-hydroxyisopropyl radical thus producing acetone and 2-iodobenzoic acid (scheme 2,

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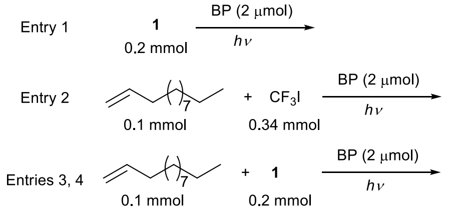
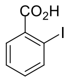
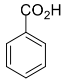
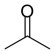
reactions A, B). The CF_3 radicals then rapidly react on *i*-PrOH to give CF_3H and regenerate the α-hydroxyisopropyl radical (reaction D), leading to an efficient radical chain cycle. That the 2-iodobenzoic acid was by far the main iodinated product obviously shows that most of the CF_3H, and thus of the CF_3 radicals generated in the reaction, do not originate from CF_3I which forms during the reaction. This is further supported by the fact that CF_3I appears to be stable in the reaction conditions, i.e. in the absence of alkene. Indeed, prolonging the irradiation (15 + 35 min) did not affect the amount of CF_3I formed after full conversion of **1**.

Table 2. Products distribution/yield under various conditions.[a]



Entry			CF_3H	CF_3I		**2a**	**3**
1[b]	80%	24%	68%	23%	100%	/	/
2[c]	/	/	16%	/	25%	40%	<2%
	/	/	35%	/	43%	60%	<2%
3[d]	120%	80%	64%	10%	192%	56%	8%
	(60%)	(40%)	(32%)	(5%)	(96%)	(28%)	(4%)
4[e]	50%	35%	5%	<5%	/	27%	6%

[a] $^1H/^{19}F$ NMR yields(± 5%, spectra recorded at 20°C). See ESI for detailed experimental conditions; [b] 15 min of irradiation; [c] 90 min (upper numbers) and 210 min (lower numbers) of irradiation. Yields with respect to 1-dodecene (limiting reagent); [d] 90 min of irradiation. Yields with respect to 1-dodecene (limiting reagent). To allow a direct comparison with entry 1 the yields with respect to **1** are given in parenthesis; [e] Same conditions than entry 3 except of using isopropanol-d8 instead of *i*-PrOH. Yields refer to 2-deutero benzoic acid, CF_3D and 3-deutero-1,1,1-trfluorotridecane.

Overall, these results suggest that the CF_3 radicals and CF_3I could derive from the decomposition of a common radical intermediate produced by the reduction of **1** by α-hydroxyisopropyl radicals (reaction A), CF_3I being produced along with acetone and the benzoic acid radical (reaction C), which then will react with *i*-PrOH to afford the benzoic acid and the α-hydroxyisopropyl radicals (reaction E).

A substantial amount of CF_3I is thus generated, i.e. potentially up to 40-50% of the initial alkene amount employed in the reaction conditions as 2 equiv. of **1** are employed. CF_3I could thus represent a potent source of CF_3 and I atom found in the products, particularly as our recent work on BP-photosensitized ATRA (ATRA = Atom Transfer Radical Additions) reactions showed that various perflluoroalkyliodides (C_4F_9I, $C_8F_{17}I$…) could be very effectively and rapidly added onto alkenes and alkynes under similar reaction conditions, except that methanol was the solvent.[16b] We then tested whether CF_3I could react as an ATRA donor in the reaction conditions. When 3.4 equiv CF_3I were reacted with the alkene, the reaction proceeded well, albeit at a slower rate (entry 2). After 90 min irradiation a satisfactory 40% yield of **2a** was obtained, if one considers that only 0.7 equiv. of CF_3I (0.27 mmol left in solution) and 0.55 equiv. of the alkene were consumed. After 210 min of irradiation the yield of **2a** reached 60% while 2.4 equiv. of CF_3I and 0.3 equiv. of 1-dodecene were still left in solution. Less CF_3H and acetone were formed compared to a reaction run from **1** (compare entries 2 and 3). Interestingly, only traces of the hydrotrifluoromethylated product were detected (< 2%), presumably because the iodine atom abstraction (reaction G) is much faster than the hydrogen atom abstraction from *i*-PrOH (reaction J).

While CF_3I generated *in situ* is a likely intermediate of the reaction, one should remember that a maximum of ~ 40-50% of CF_3I with respect to **2** is probably generated in the process. Considering this amount, that the radical chain cycle (reactions F, G) is not generating quantitatively the ATRA product (see entry 2 in table 2) due mainly to competitive side-production of CF_3H (ratio **2a**/CF_3H ~ 2.5/1 after 90 min reaction), and that up to 10% CF_3I is typically left after completion of a reaction implying the alkene (entry 3), it can be estimated that the pathway implying CF_3I could lead to a maximum ~ 30% yield of **2a**. This suggests that another pathway could be at work. Moreover, comparing the amount of the 2-iodobenzoic acid present in solution for reactions run in the absence and in the presence of alkene, clearly reveals that in the latter conditions a significant amount of 2-iodobenzoic acid is consumed, i.e corresponding to a decrease in yield of ~ 40% with respect to the alkene (compare entries 1 and 3). As there is no obvious reason that the presence of the alkene could lead to an increased production of CF_3I, and consequently to the observed "extra-consumption" of 2-iodobenzoic acid, we propose that the 2-iodobenzoic acid could serve as a "direct" iodine atom source, in particular for the intermediate secondary trifluoromethylated alkyl radical to afford the ATRA product (reaction H). Interestingly, although this reaction is endothermic, work by Dolenc and Plesničar has revealed that iodine abstraction by alkyl radicals can be very efficient in iodobenzenes ortho-substituted with bulky groups.[22] This was mostly ascribed to the steric strain release during the iodine atom elimination. Consequently, the rate of iodine abstraction by cyclohexyl radicals on 2-iodobenzoic acid was found to be ~ 15 times faster than on the benzoic acid. We propose that reaction H could account for a significant amount of the ATRA product that is produced. However, further studies will be necessary to ascertain such reactivity.

Lastly, when a reaction was conducted in isopropanol-d8 (entry 4), the reaction rate was slowed down by a factor of ~ 2. Moreover, analysis of the ^1H and ^{19}F NMR spectra showed that the deuterated fluoroform, the 2-deuterobenzoic acid and the 3-deutero-1,1,1-trfluorotridecane were formed almost exclusively, confirming that reactions D, E and J are key pathways for the generation of the reducing α-hydroxyisopropyl radicals.

In conclusion, we have described herein an operationally simple protocol to conduct iodotrifluoromethylation of alkenes which exploits a catalytic amount of benzophenone, low intensity "black light" sources, the Togni reagent **1** and

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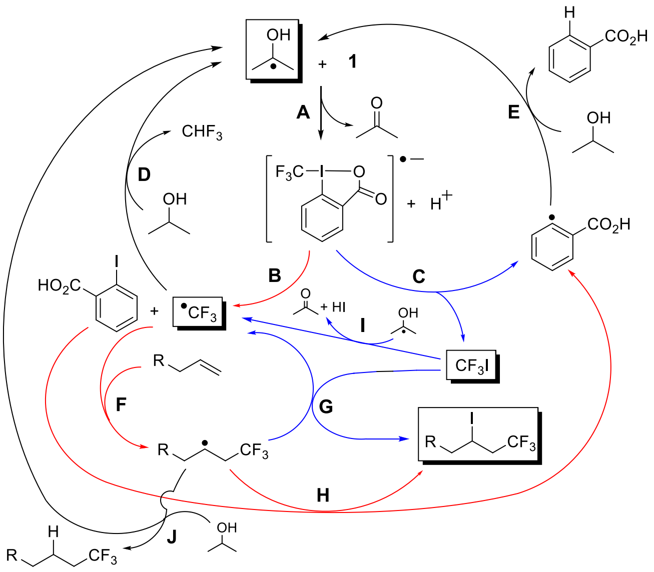
isopropanol as both solvent and source of reactive α-hydroxyisopropyl radicals. For the first time, both the trifluoromethyl group and iodine atom of Togni reagent could be integrated to a substrate with satisfactory efficiency. It was shown that this light-mediated and metal-free procedure allowed very effective generation of trifluoromethyl radicals, along with a substantial amount of iodotrifluoromethane. Preliminary studies highlight the key role played by α-hydroxyisopropyl radicals as powerful reducer of the Togni reagent, and a reaction mechanism is proposed in which both CF_3I and 2-iodobenzoic acid could directly react with the intermediate secondary trifluoromethylalkyl radical to provide the ATRA product. Studies are in progress in our group to ascertain such unusual reactivity.



Scheme 2. Proposed reaction mechanism.

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