Highly Selective Perfluoroalkylation of Unsaturated Molecules upon Photoirradiation in BTF as an Organic/Fluorous Hybrid Solvent

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Abstract: Benzotrifluoride (BTF), an eco-friendly solvent, can dissolve many organic and fluorous molecules because of the organic and fluorous motifs in its structure. Using BTF as solvent, we have developed a series of reactions for perfluoroalkylation of various unsaturated compounds upon photoirradiation with a Xe lamp through Pyrex. For example, alkynes, allenes, vinylcyclopropanes, isocyanides, diynes, dienes, and enynes successfully undergo regioselective perfluoroalkylidination, perfluoroalkylselenation, and perfluoroalkytelluration in BTF. In addition, the present photoinitiation procedure can be applied to trifluoromethylation.

Keywords: Benzotrifluoride, Perfluoroalkylation, Organic/fluorous hybrid solvent, Radical addition reaction, Atom-economical reaction.

1. INTRODUCTION

In 1997, Curran and co-worker reported that BTF (benzotrifluoride, CF₃-Ph), is in a new class of eco-friendly solvents (Figure 1) and is a useful alternative solvent for organic reactions currently conducted in dichloromethane or related solvents [1-14]. BTF has both organic and fluorous motifs in its structure and thus can dissolve both organic and fluorous molecules, so it is regarded as an organic/fluorous hybrid solvent. BTF is a clear, free-flowing liquid with a relatively low toxicity (oral, rat LD₅₀: 15000 mg/kg), a boiling point (b.p.) of 102 °C, melting point (m.p.) of -29 °C, and density of 1.2 g/mL (25 °C). Judging from the normalized empirical solvent polarity parameter $E^T_N$, BTF ($E^T_N = 0.241$) is slightly more polar than THF ($E^T_N = 0.207$) and ethyl acetate ($E^T_N = 0.228$) and slightly less polar than chloroform ($E^T_N = 0.259$) and dichloromethane ($E^T_N = 0.309$).

Fluorinated organic compounds have often been used in medicinal chemistry, agricultural chemistry, and material science, and the development of novel methods for introducing fluorinated organic groups to organic molecules is therefore of great importance [15-19]. Among the fluorinated organic molecules, perfluoroalkyl iodides (Rf-I) are expected to be potentially useful parent reagents for introducing perfluoroalkyl (fluorous) groups into organic molecules [20]. However, examples of the practical use of perfluoroalkyl iodide for this purpose are limited, because they are difficult to mix with organic molecules. As mentioned above, BTF can act as a useful organic/fluorous hybrid solvent, and therefore, we have investigated a series of radical addition reactions of perfluoroalkyl iodides to unsaturated organic molecules using BTF as solvent.

Perfluoroalkyl iodides exhibit their absorption maxima in the UV regions ($\lambda_{\text{max}} = 270$ nm, $\epsilon = 4.9 \times 10^3$), and the absorption reaches to 350 nm (see, Figure 2). Therefore, upon irradiation with UV or near-UV light, homolytic dissociation of perfluoroalkyl iodides takes place to generate perfluoroalkyl radicals (eq. 1).

$$\text{R}_f\text{I} \xrightarrow{h\nu} \text{R}_f^+ + \text{I}^- \quad (1)$$

Although several kinetic studies on the addition of Rf-I to alkenes and alkynes using the photoinitiation technique have been conducted [14], highly efficient photoinduced methods for the introduction of fluorous groups into a wide range of unsaturated compounds have remained largely undeveloped [21, 22].

This review describes our recent studies on a series of highly selective perfluoroalkylations of a wide variety of unsaturated organic molecules with simultaneous introduction of heteroatom groups, which successfully take place in BTF upon photoirradiation.
2. PERFLUOROALKYLIODINATION

2.1. Perfluoroalkyliodination of Alkynes and Alkenes

The radical addition reaction of perfluoroalkyl iodides to alkynes such as 1-octyne and phenylacetylene was examined under photoirradiation conditions in BTF as the solvent [23], and the results are summarized in Table 1. If another solvent was used instead of BTF, henicosafluorodecyl iodide, as a perfluoroalkyl iodide, was not miscible with the substrates. Therefore, the use of BTF as a solvent greatly contributes to the efficiency of the desired radical addition.

Photoinduced perfluoroalkyliodination was examined with both a W lamp and a Xe lamp. The perfluoroalkyliodination with the W lamp through Pyrex resulted in the formation of the desired perfluoroalkylated products in very low yields (entries 1 and 3), because the light intensity of the W lamp was very low in the wavelength region between 300 and 350 nm. In contrast, under the Xe lamp, which has a higher light-intensity in near-UV region than the W lamp, through Pyrex, perfluoroalkyliodination proceeds successfully to give the desired 1-perfluoroalkyl-2-iodo-1-alkenes with excellent regioselectivity (entries 2 and 4).

A possible mechanistic pathway is as follows (see Scheme 1): (i) Upon irradiation with near-UV light, $^0\text{C}_{10}\text{F}_{21}\text{I}$ undergoes homolytic dissociation to generate $^n\text{C}_{10}\text{F}_{21}\cdot$ and $\text{I}$, and the formed perfluoroalkyl radical ($^0\text{C}_{10}\text{F}_{21}\text{I}$) attacks the terminal carbon of the alkynes regioselectively. (ii) The formed vinylic radical abstracts

![Scheme 1](image-url)
an iodide atom from \(^{12}C_{10}F_{21}I\) to yield the 1-perfluoroalkyl-2-iodo-1-alkene, regenerating \(^{12}C_{10}F_{21}•\). The high \(E\)-selectivity can be explained by the iodine abstraction at the less hindered \(anti\) position of \(^{12}C_{10}F_{21}I\) against the \(^{12}C_{10}F_{21}•\).

Furthermore, the photoinduced reaction of perfluoroalkyl iodide with alkenes was examined (Scheme 2). The photoinduced reaction of 1-octene with henicosafluoro-n-decyl iodide in BTF took place successfully to give the desired iodoperfluoroalkylated product in 61% yield. Similarly, iodoperfluoroalkylation of 5-hexen-2-one and allyl alcohol afforded the desired perfluoroalkyliodination products in 56% and 45% yields, respectively, although a prolonged reaction time (18 h) was needed. In the case of aromatic alkenes such as styrene, however, the perfluoroalkyliodination did not take place efficiently, most probably owing to the instability of the benzylic iodide under the photoirradiation conditions [24]. In the case of electron-deficient alkenes such as acrylonitrile and ethyl acrylate, the polymerization of the alkenes was preferred to the desired perfluoroalkyliodination.

Scheme 2:

Table 2: Perfluoroalkyliodination of 1-phenylvinylcyclopropane

<table>
<thead>
<tr>
<th>entry</th>
<th>time, h</th>
<th>conditions</th>
<th>yield, % (^b) ([E/Z])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>Xe lamp, r.t.</td>
<td>&gt;99 [88/12]</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>Xe lamp, r.t.</td>
<td>&gt;99 [88/12]</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>fluorescent lamp, r.t.</td>
<td>57 [95/5]</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>dark, 60 °C</td>
<td>NR</td>
</tr>
<tr>
<td>5(^c)</td>
<td>2</td>
<td>Xe lamp, r.t.</td>
<td>&gt;95 [92/8]</td>
</tr>
</tbody>
</table>

\(^1\)-phenylvinylcyclopropane (0.9 mmol), \(^{12}C_{10}F_{21}I\) (0.3 mmol), BTF (0.2 mL), Xe lamp (500 W, Pyrex), r.t. \(^b\)NMR yield.; NR: no reaction. \(^c\)1-phenylvinylcyclopropane (3.6 mmol).
2.2. Perfluoroalkylation of Vinylcyclopropanes

It is known that the ring-opening process is very fast for the cyclopropylcarbinyl radical [25-30]. Therefore, the perfluoroalkylation of vinylcyclopropanes is expected to proceed via the opening of the cyclopropane ring (Scheme 3) [23].

Perfluoroalkylation of 1-phenylvinylcyclopropane with $^\text{13}$C$_{10}$F$_{21}$I successfully afforded 1-perfluoroalkyl-2-phenyl-5-iodo-2-pentene selectively in almost quantitative yield (Table 2, entry 1). In addition, the present perfluoroalkylation of vinylcyclopropanes proceeded efficiently in a shorter time (entry 2). These results clearly indicate that the ring-opening process contributes to the efficiency in perfluoroalkylation of vinylcyclopropanes compared with usual alkenes. This reaction also took place gradually upon irradiation with room light, although a prolonged reaction time was required (entry 3). In contrast, in the dark, the perfluoroalkylation did not proceed at all (entry 4). It is also possible to reduce the amount of vinylcyclopropane (1.2 equiv.) (entry 5).

Under similar conditions, the perfluoroalkylation of several other vinylcyclopropanes was conducted,

**Table 3: Photoinitiated Perfluoroalkylation of Vinylcyclopropanes$^{a,b}$**

<table>
<thead>
<tr>
<th>Entry</th>
<th>R$^1$</th>
<th>R$^2$</th>
<th>E$_T$</th>
<th>Yield, % [E/Z]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>C$<em>{10}$F$</em>{21}$</td>
<td>0.099</td>
<td>78 [69/31]</td>
</tr>
<tr>
<td>2</td>
<td>C$_6$F$_6$</td>
<td>0.108</td>
<td>75 [67/33]</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Et$_2$O</td>
<td>0.117</td>
<td>54 [70/30]</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>0.207</td>
<td>39 [72/28]</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>BTF</td>
<td>0.241</td>
<td>88 [71/29]</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>CHCl$_3$</td>
<td>0.259</td>
<td>80 [77/23]</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>DMF</td>
<td>0.404</td>
<td>47 [78/22]</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>CH$_3$CN</td>
<td>0.460</td>
<td>49 [78/31]</td>
<td></td>
</tr>
</tbody>
</table>

$^a$C$_{10}$F$_{21}$I (0.3 mmol), vinylcyclopropane (0.9 mmol), BTF (0.2 mL), Xe lamp (500 W, Pyrex), r.t., 10 h. $^b$Isolated yield.

**Table 4: Perfluoroalkylation of $t$-Butyllallene in Various Solvents$^a$**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>$E_T$</th>
<th>Yield, % [E/Z]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PhCH$_3$</td>
<td>0.099</td>
<td>78 [69/31]</td>
</tr>
<tr>
<td>2</td>
<td>C$_6$F$_6$</td>
<td>0.108</td>
<td>75 [67/33]</td>
</tr>
<tr>
<td>3</td>
<td>Et$_2$O</td>
<td>0.117</td>
<td>54 [70/30]</td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>0.207</td>
<td>39 [72/28]</td>
</tr>
<tr>
<td>5</td>
<td>BTF</td>
<td>0.241</td>
<td>88 [71/29]</td>
</tr>
<tr>
<td>6</td>
<td>CHCl$_3$</td>
<td>0.259</td>
<td>80 [77/23]</td>
</tr>
<tr>
<td>7</td>
<td>DMF</td>
<td>0.404</td>
<td>47 [78/22]</td>
</tr>
<tr>
<td>8</td>
<td>CH$_3$CN</td>
<td>0.460</td>
<td>49 [78/31]</td>
</tr>
</tbody>
</table>

$^a$C$_{10}$F$_{21}$I (0.3 mmol), 1-ethylallene (0.9 mmol), solvent (0.2 mL), Xe lamp (Pyrex), r.t., 10 h. $^b$Normalized empirical parameter of solvent polarity, based on the absorptions of a pyridinium-N-phenoxide betaine dye [33, 34, 35]. $^c$Determined by $^1$H NMR.
and the results are shown in Table 3. A variety of vinylcyclopropanes underwent efficient, selective perfluoroalkyl iodination through opening of the cyclopropane ring.

### 2.3. Perfluoroalkyl Iodination of Allenes

The successful perfluoroalkylation prompted us to examine the photoinduced perfluoroalkylation of allenes (1,2-dienes). Table 4 lists the results of perfluoroalkylation of tert-butylallene with C_{10}F_{21}I in various solvents. Upon irradiation with a Xe lamp through Pyrex, C_{10}F_{21}I added to tert-butylallene regioselectively in various solvents, and the corresponding perfluoroalkylation product, in which perfluoroalkyl and iodo groups were introduced into the terminal and central carbons of the allene, respectively, was obtained [23, 31, 32].

Nonpolar solvents (entry 1) and halogen-containing solvents (entries 2, 5, and 6) were effective for the desired perfluoroalkylation. In contrast, use of polar solvent (entries 7 and 8) resulted in the decrease in the yield of the perfluoroalkylation product. Among the solvents used, BTF provides the best result for the perfluoroalkylation. Table 5 presents the results of photoinitiated perfluoroalkylation of substituted allenes. For monosubstituted allenes, the perfluoroalkylation took place selectively at the terminal carbon-carbon double bond of the allenes to regioselectively give the corresponding β-iodoallylic perfluoroalkanes in good yields. Compared with that of monosubstituted allenes, the perfluoroalkylation of disubstituted allenes resulted in low yields of the desired addition products.

### 2.4. Perfluoroalkyl Iodination of Dienes, Diynes, and Enynes

Photoinduced perfluoroalkylation of conjugate dienes (1,3-dienes) such as 2,3-dimethyl-1,3-butadiene was also examined (Scheme 4) [23]. When the reaction of 2,3-dimethyl-1,3-butadiene with C_{10}F_{21}I was conducted under irradiation with a Xe lamp through Pyrex for 10 h in BTF, the 1,4-adduct was obtained in 33% yield along with a small amount of a byproduct. Prolonging the reaction time (18 h) increased the yield of the desired product to 55%.

Furthermore, this photolysis technique was applied to the radical cyclization of dienes, diynes, and enynes. At first, the radical cyclization reaction was conducted using C_{10}F_{21}I and diallyl ether under photolysis conditions in BTF (Scheme 5). After the reaction was completed, the corresponding iodoperfluoroalkylated cyclization product was successfully obtained in 58% yield, along with small amounts of the acyclic adduct as a byproduct. This photolysis procedure was also applicable to the radical cyclization of 1,6-heptadiene, as an example of

### Table 5: Photoinitiated Perfluoroalkylation of Allenes

<table>
<thead>
<tr>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>R&lt;sup&gt;3&lt;/sup&gt;</th>
<th>C&lt;sub&gt;10&lt;/sub&gt;F&lt;sub&gt;21&lt;/sub&gt;I</th>
<th>yield</th>
<th>regioselectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-t-Bu</td>
<td></td>
<td></td>
<td>C&lt;sub&gt;10&lt;/sub&gt;F&lt;sub&gt;21&lt;/sub&gt;I</td>
<td>88%</td>
<td>(E/Z = [63/37])</td>
</tr>
<tr>
<td>1-t-Bu</td>
<td></td>
<td></td>
<td>C&lt;sub&gt;10&lt;/sub&gt;F&lt;sub&gt;21&lt;/sub&gt;I</td>
<td>74%</td>
<td>[28/72]</td>
</tr>
<tr>
<td>1-n-Butyl</td>
<td></td>
<td></td>
<td>C&lt;sub&gt;10&lt;/sub&gt;F&lt;sub&gt;21&lt;/sub&gt;I</td>
<td>58%</td>
<td>[27/73]</td>
</tr>
<tr>
<td>1-n-Hex</td>
<td></td>
<td></td>
<td>C&lt;sub&gt;10&lt;/sub&gt;F&lt;sub&gt;21&lt;/sub&gt;I</td>
<td>65%</td>
<td>[27/73]</td>
</tr>
<tr>
<td>1-n-Hex</td>
<td></td>
<td></td>
<td>C&lt;sub&gt;10&lt;/sub&gt;F&lt;sub&gt;21&lt;/sub&gt;I</td>
<td>32%</td>
<td>[21/79]</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.9 mmol of allenes and 0.3 mmol of C_{10}F_{21}I were used in BTF (0.2 mL) upon irradiation with Xe lamp through Pyrex.

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a simple diene. In this case, the cyclic and acyclic perfluoroalkyliodination products were obtained in a ratio of 36/40. Since the rate constant \((k_c)\) for cyclization of the 5-hexenyl radical is \(2.0 \times 10^5\) s\(^{-1}\) [36-38], the rate constant for the iodine abstraction by radical intermediates from \(^{\text{n}}\)C\(_{10}\)F\(_{21}\)I is roughly estimated to be \(2.2 \times 10^5\) s\(^{-1}\). This radical-capturing ability is lower than those of \(^{\text{n}}\)Bu\(_3\)SnH or (PhSe)\(_2\) and higher than those of (Me\(_3\)Si)\(_3\)SiH or \(^{\text{n}}\)Bu\(_3\)GeH [39].

Next, the radical cyclization of diynes with perfluoroalkyl iodide in BTF was examined [40]. Upon photoirradiation with a Xe lamp through Pyrex, dipropargyl ether successfully reacted with \(^{\text{n}}\)C\(_{10}\)F\(_{21}\)I to give the corresponding cyclic perfluoroalkyliodination product in 65% yield (Scheme 6). Moreover, in the reactions of bis(propargyl)malonic acid diethyl ester and 1,6-heptadiene, the desired cyclic products were obtained with high stereoselectivity.

Finally, the radical cyclization of enynes was conducted. Table 6 presents the results of photoinduced perfluoroalkyliodination of several enynes. The photoinduced reaction of diethyl allylpropargyimalonate with \(^{\text{n}}\)C\(_{10}\)F\(_{21}\)I was completed in a short time (1 h), and the two corresponding types of five-membered cyclization products were obtained in almost quantitative yields (Table 6, entry 1). Similar

### Scheme 4:

\[
\begin{align*}
\text{X} = \text{O} & & \text{X} = \text{CH}_2 \\
\text{3 equiv} & & \text{3 equiv} \\
\end{align*}
\]

### Scheme 5:

\[
\begin{align*}
\text{X} = \text{O} & & \text{X} = \text{CH}_2 \\
\text{C(CO}_2\text{Et})_2 & & \text{CH}_2 \\
\end{align*}
\]

### Scheme 6:

\[
\begin{align*}
\text{X} = \text{O} & & \text{X} = \text{CH}_2 \\
\text{C(CO}_2\text{Et})_2 & & \text{CH}_2 \\
\end{align*}
\]
conditions could be employed for allyl propargyl ether, and, again, both cyclic vinyl iodide and alkyl iodide were obtained in 89% total yields (entry 2). When allyldipropargylamine was used, enyne cyclization proceeded to afford the desired products in moderate yield (entry 3).

2.5. Perfluoroalkylation of Isocyanides

Isocyanides are useful C1 units in organic synthesis as well as building blocks for nitrogen-containing heterocycles. Since isocyanides have an isoelectronic structure with carbon monoxide [41, 42], they can react with radical species to generate the corresponding imidoyl radicals [43-56]. While the radical addition reaction of perfluoroalkyl iodides to isocyanides with a copper reagent or radical initiators has been reported [57], photoinduced perfluoroalkylation has not been developed. Therefore, photoinduced perfluoroalkylation of isocyanide was examined next. When cyclohexyl isocyanide was used as a substrate for perfluoroalkylation upon photoirradiation in BTF, the corresponding 1-iodo-1-perfluoroalkylated product was obtained successfully in 92% yield (Scheme 7). This perfluoroalkylated imidoyl iodide is a promising building block for perfluoroalkylation by substitution of the iodo group with various nucleophiles.

3. PERFLUOROALKYLCHALCOGENATION

Unique reactions based on the different characteristic features of disulfides and diselenides in radical reactions have already been reported, such as
the thioselenation of alkynes [58], alkenes [59, 60], allenes [61], enynes [58], and vinylcyclopropanes [62]. These reactions clearly demonstrate the efficacy of mixed heteroatom systems for the highly selective introduction of two (or more) heteroatom functional groups into organic molecules [55, 63-65].

The rate constant for the iodine abstraction of radical intermediates from $^7\text{C}_{10}\text{F}_{21}\text{I}$ was roughly estimated to be $2.2 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ using the 5-hexenyl radical clock system (see Scheme 7), and the rate constant for the $\text{S}_\text{2}$ reaction of 5-hexenyl radical with (PhSe)$_2$ is reported to be $1.2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ [66, 67]. Therefore, PhSe-group abstraction is about 50 times faster than the iodine transfer. Furthermore, $^7\text{C}_{10}\text{F}_{21}\text{•}$ is more reactive toward unsaturated compounds than PhSe•. With these kinetic considerations in mind, a highly selective perfluoroalkylselenation of terminal alkynes using a R$_f$-I–(PhSe)$_2$ binary system has been designed [68].

When phenylacetylene was used as the substrate, the desired perfluoroalkyliodination proceeded efficiently to give the adduct bearing perfluoroalkyl and

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent (0.5 mL)</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>neat</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>CD$_3$CN</td>
<td>68</td>
</tr>
<tr>
<td>3</td>
<td>DMF</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>CDCl$_3$</td>
<td>26</td>
</tr>
<tr>
<td>5</td>
<td>BTF</td>
<td>41</td>
</tr>
<tr>
<td>6</td>
<td>benzene</td>
<td>7</td>
</tr>
</tbody>
</table>

$^a$Phenytaclrylene (0.1 mL), (PhTe)$_2$ (0.02 mmol), $^7\text{C}_{6}\text{F}_{13}\text{I}$ (0.01 mmol), hv: high pressure Hg lamp through a filter (>400 nm). $^b$Determined by $^1$H NMR.
phenylseleno groups at the terminal and internal positions of the alkyne, respectively, with excellent regioselectivity. Table 7 lists the results of the photoinduced perfluoroalkylselenation of several terminal alkynes. Aromatic alkynes bearing methyl or bromo groups in the \( p \)-position could be utilized for this perfluoroalkylselenation, as can 1-ethynylcyclohexene. However, with aliphatic alkynes such as 1-dodecyne, the reaction did not proceed at all, because of the differences in stability of the corresponding vinylic radical intermediates. Aliphatic alkynes generate \( \sigma \)-vinyl radical intermediates, whereas aromatic alkynes generate more stable \( \pi \)-vinyl radicals [69, 70].

Moreover, the perfluoroalkyltelluration was also examined by using \( R_f-I-(\text{PhTe})_2 \) binary system [71]. First, we examined the perfluoroalkyltelluration of phenylacetylene in several solvents, as shown in Table 8. Among the solvents employed, acetonitrile is the best for the perfluoroalkyltelluration (entry 2). The perfluoroalkyltelluration in BTF provided a moderate yield of the desired adduct (entry 5).

These results indicate that \( \text{C}_6\text{F}_{13}\text{I} \) is soluble in organic solvents because it has fewer fluorine atoms than \( \text{C}_{10}\text{F}_{21}\text{I} \). Under optimized conditions, the perfluoroalkyltelluration took place smoothly to give the perfluoroalkyltelluration product regio- and stereoselectively (Table 9).

A possible pathway for the present perfluoroalkylchalcogenation may be as follows: (i) \((\text{PhCh})_2\) mainly undergoes homolytic cleavage upon photoradiation to generate \( \text{PhCh} \cdot \), because the absorption of \((\text{PhCh})_2\) is stronger than that of \( R_f-I \) (Figure 2). (ii) The formed chalcogeno radical abstracts an iodine atom from \( R_f-I \) to generate \( R_f \cdot \). (iii) \( R_f \cdot \) attacks the terminal carbon of the alkynes to form vinylic radical intermediates. (iv) The formed vinyl radical intermediates are trapped selectively by \((\text{PhCh})_2\) to give the perfluoroalkylchalcogenation products (Scheme 8).

![Scheme 8:](image-url)
4. TRIFLUOROMETHYLIODINATION

For the synthesis of fluorinated drugs, development of a reaction for the selective introduction of a trifluoromethyl group to organic molecules is of great importance [72, 73, 74]. Therefore, we examined the photoinduced trifluoromethyliodination of several unsaturated compounds (Scheme 9). The photoinduced trifluoromethyliodination of cyclohexenyllene with CF₃I (bp. -22 °C) at -22 °C in BTF led to the regioselective formation of the corresponding trifluoromethyliodination product in 26% yield [23]. Furthermore, the photoinduced reaction of vinylcyclopropane with CF₃I in BTF successfully afforded the 5-iodo-1-trifluoromethylated product in 81% yield via the ring opening of the cyclopropane. From the reaction with cyclohexylisocyanide, the 1-iodo-1-trifluoromethylated product was obtained in 68% yield. The obtained trifluoromethylated imidoyl iodide is expected to be a useful reagent for introduction of the CF₃-C(=O) group to organic molecules.

5. CONCLUSION

A highly selective method for introducing perfluoroalkyl groups into unsaturated compounds by...
using BTF as a solvent has been developed. The application of these photoinduced radical addition reactions to unsaturated bonds of alkenes, allenes, vinylic alcohols, iso- and diynes, dienes, and enynes provides useful tools for synthesizing perfluoroalkylated compounds. In particular, the photoinduced reaction of trifluoromethyl iodide in BTF affords compounds bearing a trifluoromethyl group. Furthermore, the novel photoinduced perfluoroalkylation and tellurination of alkenes by using $\text{R}_3\text{I}-(\text{PhSe})_2$ or $\text{R}_3\text{I}-(\text{PhTe})_2$ binary systems have been developed. Thus, a wide range of perfluoroalkylated compounds can be synthesized successfully. These results clearly demonstrate the efficacy of BTF as an organic/fluorous hybrid solvent in fluorous synthesis.

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Received on 12-08-2013  Accepted on 21-08-2013  Published on 31-08-2013

DOI: http://dx.doi.org/10.6000/1929-5030.2013.02.03.3

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