

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 fluorine molecules because of the organic and fluorine 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 perfluoroalkylation, perfluoroalkylselenation, and perfluoroalkyltelluration 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, $\text{CF}_3\text{-Ph}$), 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 fluorine motifs in its structure and thus can dissolve both organic and fluorine 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 LD_{50} : 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 ($E_T^N = 0.309$).

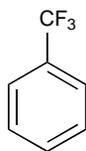
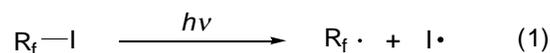


Figure 1: Structure of BTF (Benzotrifluoride).

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 ($\text{R}_f\text{-I}$) 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.

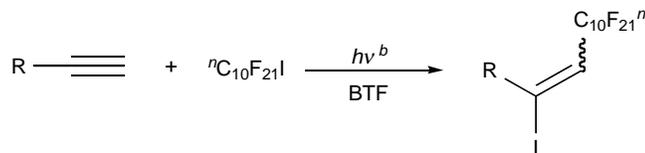
Perfluoroalkyl iodides exhibit their absorption maxima in the UV regions ($\lambda_{\text{max}} = 270 \text{ nm}$, $\epsilon = 4.9 \times 10^4$), and the absorption reaches to 350 nm (see, Figure 2). Therefore, upon irradiation with UV or near-UV light, homolytic dissociation of perfluoroalkyl iodides takes place to generate perfluoroalkyl radicals (eq. 1).



Although several kinetic studies on the addition of $\text{R}_f\text{-I}$ to alkenes and alkynes using the photoinitiation technique have been conducted [14], highly efficient photoinduced methods for the introduction of fluorine 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.

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Table 1: Perfluoroalkyl Iodination Upon Photoirradiation^a

| entry | R | condition | yield, % |
|-------|---|------------------------------|-----------------|
| 1 | ⁿ C ₆ H ₁₃ (3 equiv) | W lamp (500 W), 45 °C, 10 h | 27 |
| 2 | ⁿ C ₆ H ₁₃ (3 equiv) | Xe lamp (500 W), 45 °C, 10 h | 99 ^c |
| 3 | Ph (3 equiv) | W lamp (500 W), 45 °C, 10 h | 7 |
| 4 | Ph (3 equiv) | Xe lamp (500 W), 45 °C, 10 h | 38 ^d |

^a ⁿC₁₀F₂₁I (1 mmol, 1 M). ^b Through Pyrex (>300 nm). ^c E/Z = 85/15. ^d E/Z = 72/28.

2. PERFLUOROALKYL IODINATION

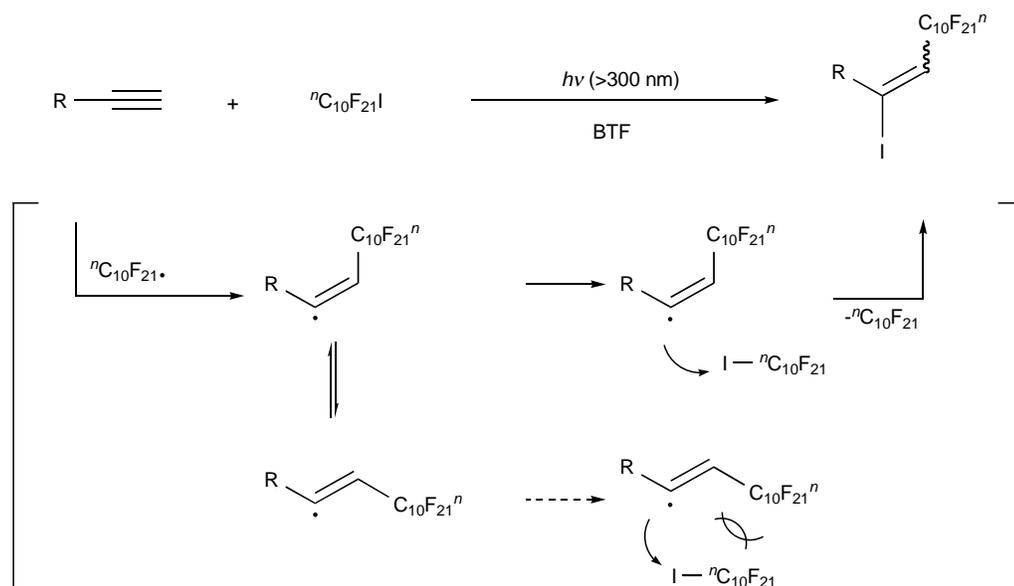
2.1. Perfluoroalkyl iodination of Alkynes and Alkenes

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, heneicosfluorodecyl 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.

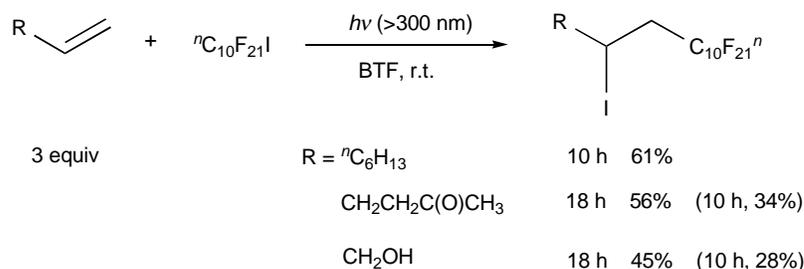
Photoinduced perfluoroalkyl iodination was examined with both a W lamp and a Xe lamp. The

perfluoroalkyl iodination 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, perfluoroalkyl iodination 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, ⁿC₁₀F₂₁I undergoes homolytic dissociation to generate ⁿC₁₀F₂₁• and I•, and the formed perfluoroalkyl radical (ⁿC₁₀F₂₁•) attacks the terminal carbon of the alkynes regioselectively. (ii) The formed vinylic radical abstracts



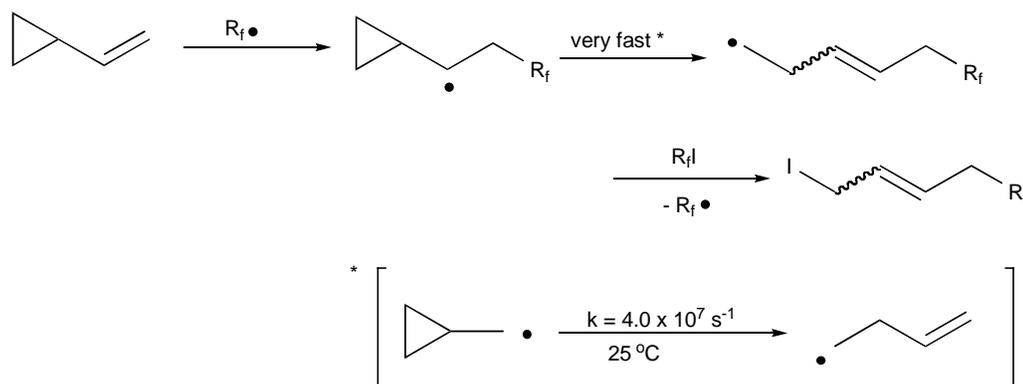
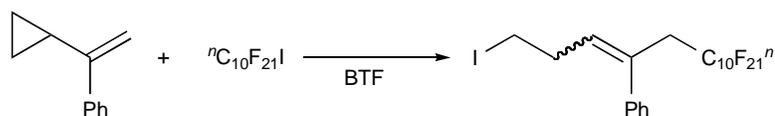
Scheme 1:

**Scheme 2:**

an iodide atom from ${}^n\text{C}_{10}\text{F}_{21}\text{I}$ to yield the 1-perfluoroalkyl-2-iodo-1-alkene, regenerating ${}^n\text{C}_{10}\text{F}_{21}\cdot$. The high *E*-selectivity can be explained by the iodine abstraction at the less hindered *anti* position of ${}^n\text{C}_{10}\text{F}_{21}\cdot$ against the ${}^n\text{C}_{10}\text{F}_{21}\cdot$.

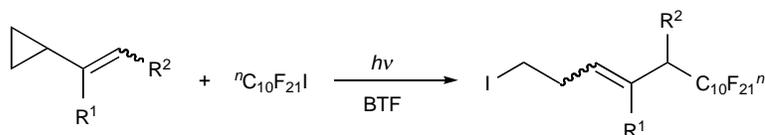
Furthermore, the photoinduced reaction of perfluoroalkyl iodide with alkenes was examined (Scheme 2). The photoinduced reaction of 1-octene with hencosafluoro-*n*-decyl iodide in BTF took place successfully to give the desired iodoperfluoroalkylated product in 61% yield. Similarly, iodoperfluoroalkylation

of 5-hexen-2-one and allyl alcohol afforded the desired perfluoroalkyl iodination 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 perfluoroalkyl iodination 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 perfluoroalkyl iodination.

**Scheme 3:****Table 2: Perfluoroalkyl iodination of 1-phenylvinylcyclopropane^a**

| entry | time, h | conditions | yield, % ^b [<i>E/Z</i>] |
|----------------|---------|------------------------|--------------------------------------|
| 1 | 4 | Xe lamp, r.t. | >99 [88/12] |
| 2 | 0.5 | Xe lamp, r.t. | >99 [88/12] |
| 3 | 100 | fluorescent lamp, r.t. | 57 [95/5] |
| 4 | 10 | dark, 60 °C | NR |
| 5 ^c | 2 | Xe lamp, r.t. | >95 [92/8] |

^a1-phenylvinylcyclopropane (0.9 mmol), ${}^n\text{C}_{10}\text{F}_{21}\text{I}$ (0.3 mmol), BTF (0.2 mL), Xe lamp (500 W, Pyrex), r.t. ^bNMR yield.; NR: no reaction. ^c1-phenylvinylcyclopropane (3.6 mmol).

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

| | | |
|--|--|--|
| | | |
| | | |

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

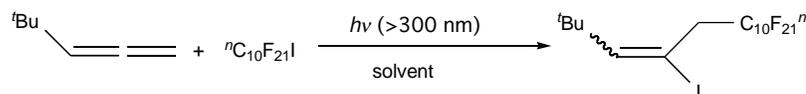
2.2. Perfluoroalkylation of Vinylcyclopropanes

It is known that the ring-opening process is very fast for the cyclopropylcarbanyl 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 $n\text{C}_{10}\text{F}_{21}\text{I}$ 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 4: Perfluoroalkylation of *t*-Butylallene in Various Solvents^a

| entry | solvent | $E_T^{N^b}$ | yield, % [E/Z] ^c |
|-------|-------------------------------|-------------|-----------------------------|
| 1 | PhCH ₃ | 0.099 | 78 [69/31] |
| 2 | C ₆ F ₆ | 0.108 | 75 [67/33] |
| 3 | Et ₂ O | 0.117 | 54 [70/30] |
| 4 | THF | 0.207 | 39 [72/28] |
| 5 | BTF | 0.241 | 88 [71/29] |
| 6 | CHCl ₃ | 0.259 | 80 [77/23] |
| 7 | DMF | 0.404 | 47 [78/22] |
| 8 | CH ₃ CN | 0.460 | 49 [78/31] |

^a $n\text{C}_{10}\text{F}_{21}\text{I}$ (0.3 mmol), *t*-butylallene (0.9 mmol), solvent (0.2 mL), Xe lamp (Pyrex), r.t., 10 h. ^bNormalized empirical parameter of solvent polarity, based on the intramolecular CT absorption of a pyridinium-*N*-phenoxide betaine dye [33, 34, 35]. ^cDetermined by ¹H NMR.

and the results are shown in Table 3. A variety of vinylcyclopropanes underwent efficient, selective perfluoroalkyliodination through opening of the cyclopropane ring.

2.3. Perfluoroalkyliodination of Allenes

The successful perfluoroalkyliodination prompted us to examine the photoinduced perfluoroalkyliodination of allenes (1,2-dienes). Table 4 lists the results of perfluoroalkyliodination of *t*-butyllallene with ${}^n\text{C}_{10}\text{F}_{21}\text{I}$ in various solvents. Upon irradiation with a Xe lamp through Pyrex, ${}^n\text{C}_{10}\text{F}_{21}\text{I}$ added to *t*-butyllallene regioselectively in various solvents, and the corresponding perfluoroalkyliodination 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 perfluoroalkyliodination. In contrast, use of polar solvent (entries 7 and 8) resulted in the decrease in the yield of the perfluoroalkyliodination product. Among the solvents used, BTF provides the best result for the perfluoroalkyliodination. Table 5 presents the results of photoinduced perfluoroalkyliodination of substituted allenes. For monosubstituted allenes, the perfluoroalkyliodination took place selectively at the terminal carbon-carbon double bond of the allenes to

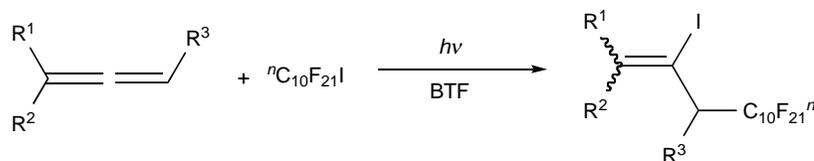
regioselectively give the corresponding β -iodoallylic perfluoroalkanes in good yields. Compared with that of monosubstituted allenes, the perfluoroalkyliodination of disubstituted allenes resulted in low yields of the desired addition products.

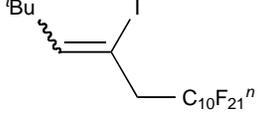
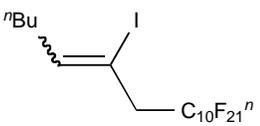
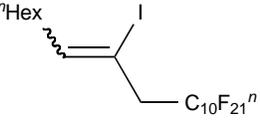
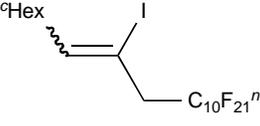
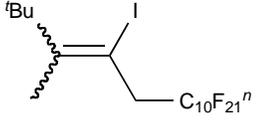
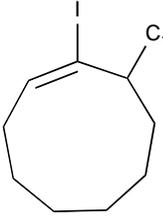
2.4. Perfluoroalkyliodination of Dienes, Diynes, and Enynes

Photoinduced perfluoroalkyliodination 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 ${}^n\text{C}_{10}\text{F}_{21}\text{I}$ 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%.

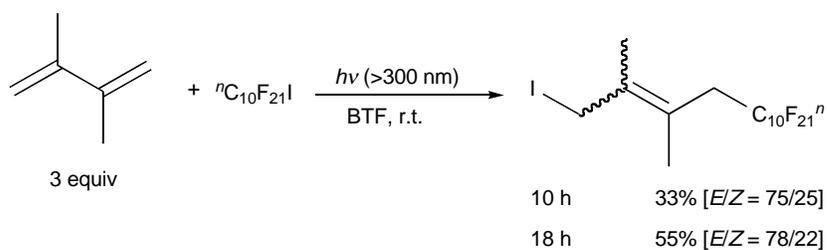
Furthermore, this photoirradiation technique was applied to the radical cyclization of dienes, diynes, and enynes. At first, the radical cyclization reaction was conducted using ${}^n\text{C}_{10}\text{F}_{21}\text{I}$ and diallyl ether under photoirradiation conditions in BTF (Scheme 5). After the reaction 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 photoirradiation procedure was also applicable to the radical cyclization of 1,6-heptadiene, as an example of

Table 5: Photoinitiated Perfluoroalkyliodination of Allenes

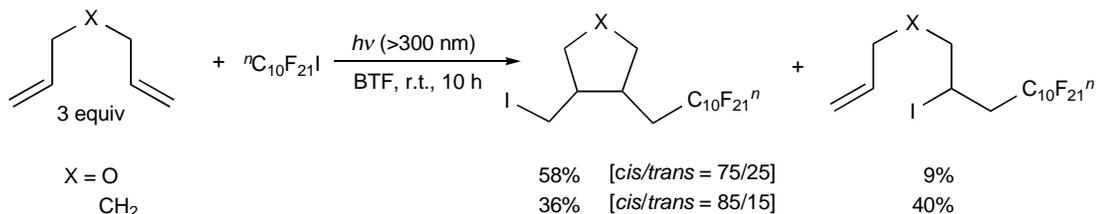


| | | |
|--|--|--|
|  88% (<i>E/Z</i> = [63/37]) |  74% [28/72] |  58% [27/73] |
|  65% [27/73] |  32% [21/79] |  14% |

Reaction conditions: 0.9 mmol of allenes and 0.3 mmol of ${}^n\text{C}_{10}\text{F}_{21}\text{I}$ were used in BTF (0.2 mL) upon irradiation with Xe lamp through Pyrex.



Scheme 4:



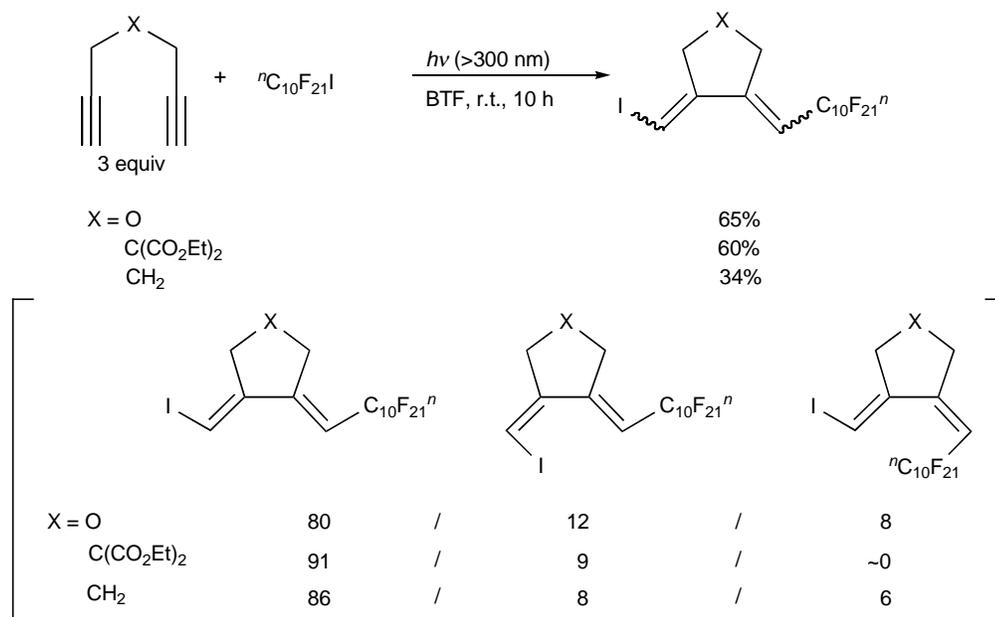
Scheme 5:

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

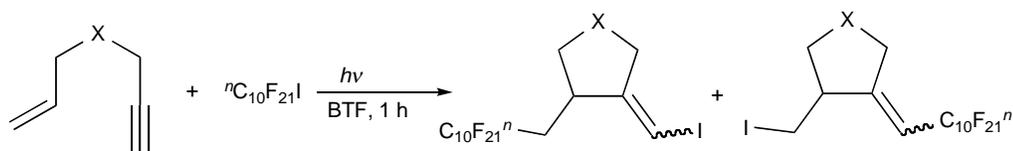
Next, the radical cyclization of diynes with perfluoroalkyl iodide in BTF was examined [40]. Upon photoirradiation with a Xe lamp through Pyrex, dipropargyl ether successfully reacted with $^{n}\text{C}_{10}\text{F}_{21}\text{I}$ to

give the corresponding cyclic perfluoroalkyl iodination 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 perfluoroalkyl iodination of several enynes. The photoinduced reaction of diethyl allylpropargylmalonate with $^{n}\text{C}_{10}\text{F}_{21}\text{I}$ 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 6:

Table 6: Photoinitiated Perfluoroalkyliodination of Various Enynes^a

| entry | enyne | product | yield, % [product ratio] |
|----------------------------------|-------|---------|--------------------------|
| 1 | | | >99 [75/25] |
| 2 | | | 89 [73/27] |
| 3 ^c 4 ^c | | | 35 47 ^b |

^aReaction conditions: 0.45 mmol of enynes and 0.15 mmol of ⁿC₁₀F₂₁I were used in the presence of BTF (0.1 mL). ^bReaction was conducted for 10 h. ^cProduct ratio was not determined.

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).

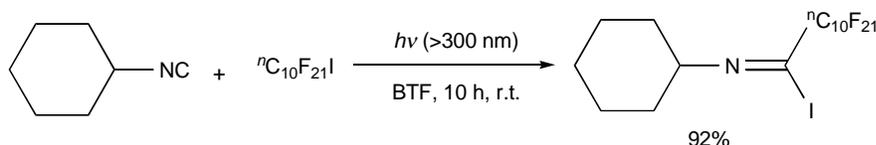
2.5. Perfluoroalkyliodination of Isocyanides

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

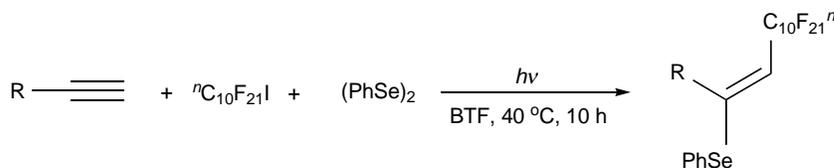
[57], photoinduced perfluoroalkyliodination has not been developed. Therefore, photoinduced perfluoroalkyliodination of isocyanide was examined next. When cyclohexyl isocyanide was used as a substrate for perfluoroalkyliodination upon photoirradiation in BTF, the corresponding 1-iodo-1-perfluoroalkylated 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.

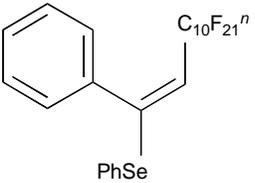
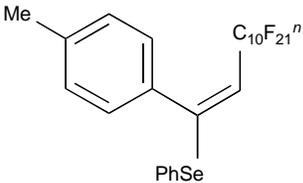
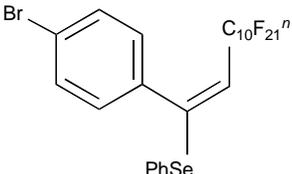
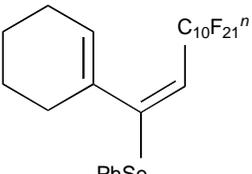
3. PERFLUOROALKYLCHALCOGENATION

Unique reactions based on the different characteristic features of disulfides and diselenides in radical reactions have already been reported, such as



Scheme 7:

Table 7: Perfluoroalkylselenation of Terminal Alkynes^{a,b}

| | |
|--|--|
|  <p>82%</p> |  <p>81%</p> |
|  <p>63%</p> |  <p>71%</p> |

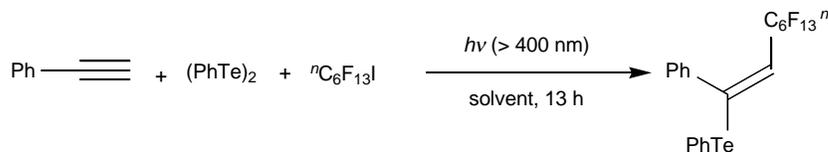
^a ${}^n\text{C}_{10}\text{F}_{21}\text{I}$ (0.1 mmol), acetylene (2 equiv), $(\text{PhSe})_2$ (2 equiv), $h\nu$: xenon lamp (Pyrex). ^bNMR yield.

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 ${}^n\text{C}_{10}\text{F}_{21}\text{I}$ 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 $\text{S}_{\text{H}}2$ reaction of 5-hexenyl radical with

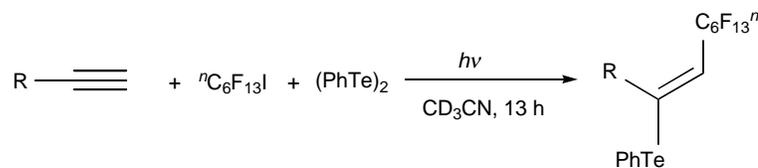
$(\text{PhSe})_2$ is reported to be $1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [66, 67]. Therefore, PhSe-group abstraction is about 50 times faster than the iodine transfer. Furthermore, ${}^n\text{C}_{10}\text{F}_{21}\bullet$ is more reactive toward unsaturated compounds than $\text{PhSe}\bullet$. With these kinetic considerations in mind, a highly selective perfluoroalkylselenation of terminal alkynes using a $\text{R}_f\text{-I}-(\text{PhSe})_2$ binary system has been designed [68].

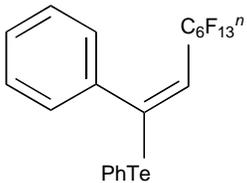
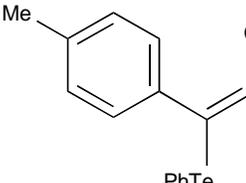
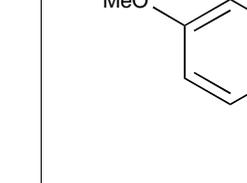
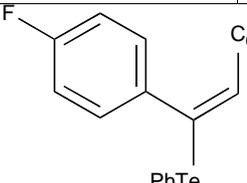
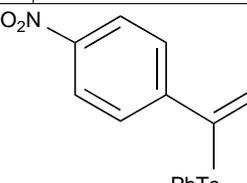
When phenylacetylene was used as the substrate, the desired perfluoroalkylodination proceeded efficiently to give the adduct bearing perfluoroalkyl and

Table 8: Perfluoroalkyltelluration of Phenylacetylene in Several Solvent^a

| entry | solvent (0.5 mL) | Yield, % |
|-------|------------------------|----------|
| 1 | neat | 23 |
| 2 | CD_3CN | 68 |
| 3 | DMF | 45 |
| 4 | CDCl_3 | 26 |
| 5 | BTF | 41 |
| 6 | benzene | 7 |

^aPhenylacetylene (0.1 mL), $(\text{PhTe})_2$ (0.02 mmol), ${}^n\text{C}_6\text{F}_{13}\text{I}$ (0.01 mmol), $h\nu$: high pressure Hg lamp through a filter (>400 nm). ^bDetermined by ^1H NMR.

Table 9: Perfluoroalkyltellation of Terminal Alkynes^a

| | | |
|--|--|--|
|  68% |  70% |  56% |
|  50% |  11% | |

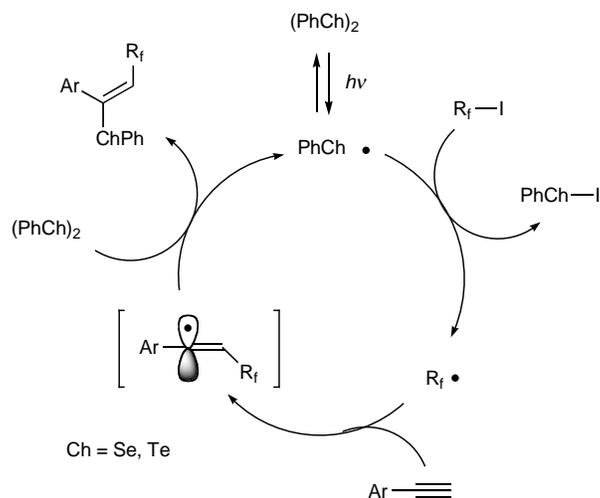
^a ${}^n\text{C}_6\text{F}_{13}\text{I}$ (0.01 mmol), acetylene (excess), $(\text{PhTe})_2$ (2 equiv), $h\nu$: high pressure Hg lamp through a filter (>400 nm).

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 σ -vinyl radical intermediates, whereas aromatic alkynes generate more stable π -vinyl radicals [69, 70].

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

These results indicate that ${}^n\text{C}_6\text{F}_{13}\text{I}$ is soluble in organic solvents because it has fewer fluorine atoms than ${}^n\text{C}_{10}\text{F}_{21}\text{I}$. Under optimized conditions, the perfluoroalkyltellation took place smoothly to give the perfluoroalkyltellation 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 photoirradiation to generate $\text{PhCh}\cdot$, because the absorption of $(\text{PhCh})_2$ is stronger than that of R_fI (Figure 2). (ii) The formed chalcogeno radical abstracts an iodine atom from R_fI to generate $\text{R}_f\cdot$. (iii) $\text{R}_f\cdot$ 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:**

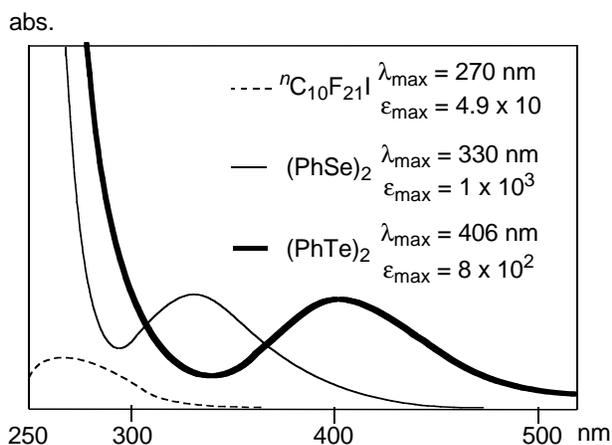


Figure 2: UV-Visible Spectra of $n\text{C}_{10}\text{F}_{21}\text{I}$, $(\text{PhSe})_2$ and $(\text{PhTe})_2$.

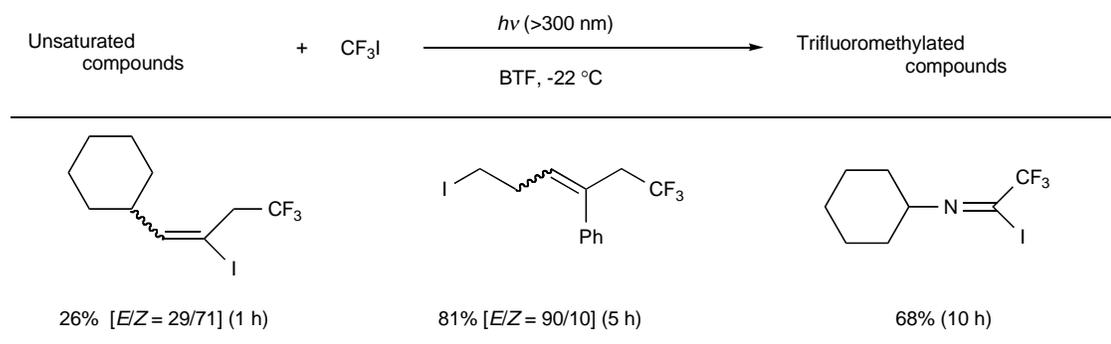
4. TRIFLUOROMETHYLIODINATION

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 cyclohexallene with CF_3I (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 CF_3I 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 $\text{CF}_3\text{-C(=O)}$ group to organic molecules.

5. CONCLUSION

A highly selective method for introducing perfluoroalkyl groups into unsaturated compounds by



Reaction conditions: 0.3 mmol of and excess amount of CF_3I were used in the presence of BTF.

Scheme 9:

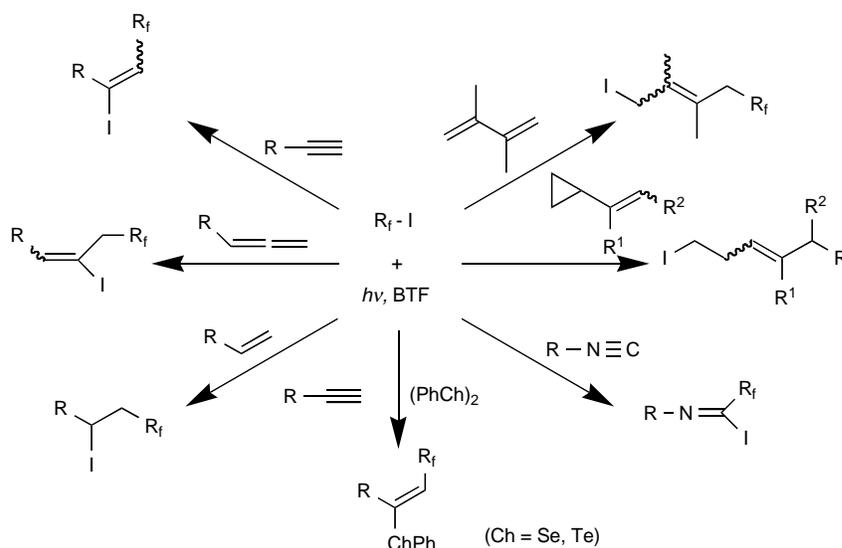


Figure 3: Perfluoroalkylation in BTF.

using BTF as a solvent has been developed. The application of these photoinduced radical addition reactions to unsaturated bonds of alkynes, allenes, vinylcyclopropanes, isocyanides, 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 perfluoroalkyl-selenation and -telluration of alkynes by using $R_f-I-(PhSe)_2$ or $R_f-I-(PhTe)_2$ 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 a organic/fluorous hybrid solvent in fluorous synthesis.

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