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Highly regioselective iodoperfluoroalkylation of allenes with perfluoroalkyl iodides upon irradiation with near-UV light

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Abstract—Upon irradiation through Pyrex with a xenon lamp (*hν*>300 nm), perfluoroalkyl iodides add to terminal allenes regioselectively to afford the corresponding iodoperfluoroalkylated products, where perfluoroalkyl and iodo groups are selectively introduced into the terminal and central carbons of allenes, respectively. © 2001 Elsevier Science Ltd. All rights reserved.

In view of the growing interest in fluorinated organic compounds in material science, medicinal chemistry, and organic synthesis,[1] the development of useful methods for efficient and selective introduction of fluorine-containing functions into organic molecules is of great importance. Perfluoroalkyl iodides (Rf-I) are one of the most useful perfluoroalkylating reagents for various organic molecules, and, for example, the iodoperfluoroalkylation of carbon–carbon unsaturated compounds such as alkenes and alkynes proceeds by a radical-chain mechanism initiated by various radical initiators.[1] Since perfluoroalkyl iodides exhibit their absorption in UV and near-UV regions (Fig. 1), the photoinitiation based on the homolytic dissociation of Rf-I is also applicable for the iodoperfluoroalkylation of unsaturated compounds with Rf-I. Indeed, many kinetic studies of the addition of Rf-I to alkenes and alkynes have been conducted by using the photoinitiation technique.[1] However, the application of the photoinitiation to synthetic chemistry of organofluorous compounds has remained largely undeveloped,[2] most probably due to the prejudice that the photoinitiation is an inefficient process. Herein we report that the xenon-lamp-irradiation causes efficient iodoperfluoroalkylation of allenes with Rf-I, giving the corresponding β-iodoallylic perfluoroalkanes regioselectively in good yields (Eq. (1)).[3]

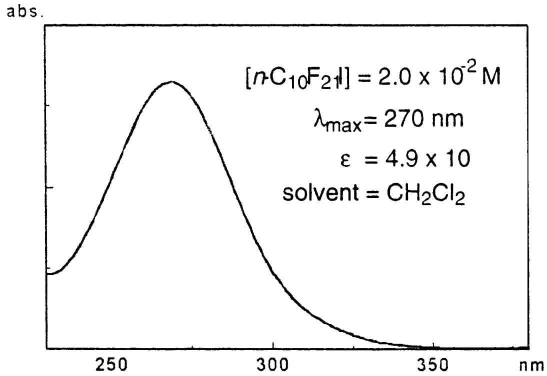

Figure 1. UV–vis spectrum of *n*-$C_{10}F_{21}I$.

Upon irradiation with a xenon lamp (500 W) through Pyrex (*hν*>300 nm), the reaction of *t*-butylallene (**1a**, 0.9 mmol) with heneicosafluoro-*n*-decyl iodide (0.3 mmol) in BTF[4] (0.2 mL) was conducted at ambient

Table 1. Perfluoroalkylation of *t*-butylallane[a]

Conditions	Yield (%) [*E*/*Z*]
hν (tungsten lamp), 4 h	4 [82/18]
hν (Xe lamp), 1 h	17 [80/20]
hν (Xe lamp), 2 h	49 [77/23]
hν (Xe lamp), 4 h	83 [68/32]
hν (Xe lamp), 10 h	88 [63/37]
Dark, 10 h, 60°C	No reaction

[a] *n*-$C_{10}F_{21}I$ (0.3 mmol), **1a** (0.9 mmol), BTF (0.2 mL).

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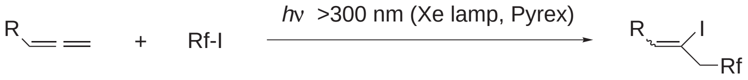
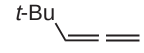
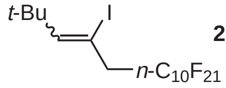
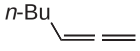
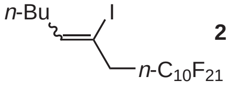
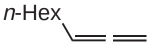
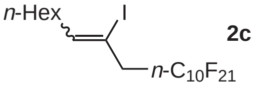
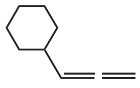
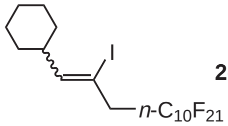
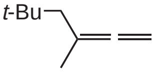
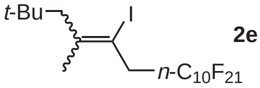
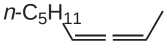
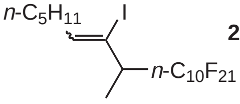
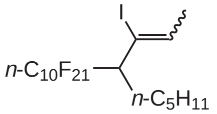
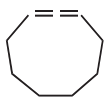
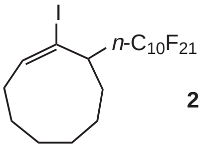


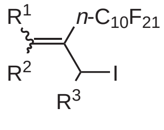
(1)

temperature for 4 h. The corresponding iodoperfluoroalkylated product (**2a**),[5] in which perfluoroalkyl and iodo groups were regioselectively introduced into the terminal and central carbons of **1a**, respectively, was obtained in 83% yield (Eq. (2) and Table 1). On the other hand, the use of a tungsten lamp in place of the xenon lamp resulted in the formation of **2a** in a very low yield. This is most probably because the tungsten lamp can not irradiate the light of wavelength between 300 and 330 nm intensively, compared with the xenon lamp. In the dark, the desired iodoperfluoroalkylation did not proceed at all. The influence of solvent on this iodoperfluoroalkylation of **1a** was investigated as follows: (yield of **2a** [*E*/*Z*], solvent, polarity of the solvent (E_T^N)[6]) = (78% [69/31], toluene, 0.099); (75% [67/33], C_6F_6, 0.108); (79% [67/33], benzene, 0.111); (54% [70/30], Et_2O, 0.117); (39% [72/28], THF, 0.207); (83% [68/32], BTF, 0.241); (80% [77/23], $CHCl_3$, 0.259); (47%

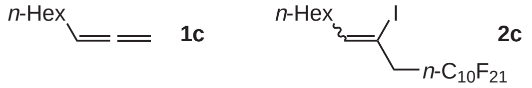
Table 2. Iodoperfluoroalkylation of allenes[a]

Entry	Allene, **1**				Yield, % [*E* / *Z*]
1		**1a**		**2a**	88 [63 / 37]
2		**1b**		**2b**	75 [28 / 72]
3		**1c**		**2c**	58 [27 / 73]
4		**1d**		**2d**	65 [27 / 73]
5		**1e**		**2e**	32 [21 / 79][b]
6		**1f**		**2f**	12 [20 / 80][c]
				**2f'**	7 [27 / 73][d]
7		**1g**		**2g**	14[e]

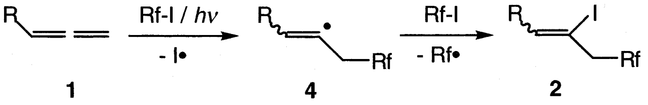
[a] Reaction conditions : n-$C_{10}F_{21}I$ (0.3 mmol), allene (0.9 mmol), BTF (0.2 mL), hν (Xe lamp, Pyrex), r.t., 10 h. [b] Accompanied by the formation of trace amounts of the regioisomer (**3e**)). [c] Accompanied by the formation of the regioisomer (**3f**, 3% [*E*/*Z* = 49/51]). [d] Accompanied by the formation of trace amounts of the regioisomer (**3f'**). [e] Accompanied by the formation of the regioisomer (**3g**, 9%).



3e (R^1 = t-$BuCH_2$, R^2 = CH_3, R^3 = H)
3f (R^1 = n-C_5H_{11}, R^2 = H, R^3 = CH_3)
3f' (R^1 = CH_3, R^2 = H, R^3 = n-C_5H_{11})
3g (R^1 = H, R^2-R^3 = -$(CH_2)_6$-)

3 

58 [27 / 73] (2)



Scheme 1.

[78/22], DMF, 0.404); (13% [77/23], DMSO, 0.444); (49% [78/32], CH_3CN, 0.460). These results strongly suggest that nonpolar solvents such as toluene and benzene or halogen-containing solvents such as C_6F_6, BTF, and $CHCl_3$ are effective for the iodoperfluoroalkylation. Even in the absence of solvent, the photoinitiated iodoperfluoroalkylation of **1a** proceeds successfully to give rise to 73% of **2a** ($E/Z=66/34$).

Table 2 represents the results of photoinduced iodoperfluoroalkylation of substituted allenes.[7] In the case of monosubstituted allenes (**1a**–**d**), the iodoperfluoroalkylation took place selectively at the terminal carbon–carbon double bond of the allenes to give the corresponding β-iodoallylic perfluoroalkanes (**2a**–**d**) in good yields (entries 1–4). Compared with monosubstituted allenes, the iodoperfluoroalkylation of disubstituted allenes (**2e**–**g**) resulted in the formation of the iodoperfluoroalkylated products in lower yields. 1,1-Disubstituted allene (**1e**) provided the corresponding iodoperfluoroalkylated product (**2e**) regioselectively (entry 5), whereas the iodoperfluoroalkylation of internal allenes (**1f** and **1g**) proceeded with the formation of regioisomers (**3f**, **3f′**, and **3g**, respectively) (entries 6 and 7). Iodoperfluoroalkylation of allene itself with *n*-$C_{10}F_{21}I$ also took place at refluxing temperature of allene (−34°C) upon irradiation with a xenon lamp, providing the corresponding adduct ($CH_2=C(I)CH_2C_{10}F_{21}$-*n*) regioselectively in 20% yield (the reaction conditions were not optimized).

Next we examined the iodoperfluoroalkylation employing some other iodofluoroalkanes. The photoinduced reaction of *n*-C_4F_9I with *t*-butylallene (**1a**) and 1,2-nonadiene (**1c**) under similar reaction conditions successfully afforded the corresponding adducts (R-$CH=C(I)CH_2C_4F_9$-*n*, R = *t*-Bu and *n*-Hex) regioselectively in 76 and 59% yields, respectively. Moreover, the photoinduced iodotrifluoromethylation of cyclohexylallene (**1d**) with CF_3I (bp −22.5°C) at −22.5°C led to the regioselective formation of 2-iodo-3-trifluoromethylpropene ($E/Z=29/71$) in 26% yield (the reaction conditions were not optimized).

A possible mechanistic pathway may include the following (Scheme 1): (i) irradiation with near-UV light causes homolytic dissociation to generate Rf$^\bullet$ and I$^\bullet$, the former radical of which attacks the kinetically favorable terminal carbon of allenes regioselectively, forming a vinylic radical intermediate (**4**); (ii) the vinylic radical (**4**) abstracts an iodide atom from Rf-I to produce iodoperfluoroalkylated product (**2**) with regeneration of Rf$^\bullet$. In the case of inner allenes, Rf$^\bullet$ also attacks the thermodynamically favorable central carbon of allenes competitively, probably due to the steric effect of the substituents.

In summary, the radical addition of Rf-I to a variety of substituted allenes is revealed for the first time.[3] In this iodoperfluoroalkylation of allenes, the xenon-lamp-irradiation is a convenient and useful procedure for introducing perfluoroalkyl groups into allenes. Further study along these lines is now in progress.

Acknowledgements

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5. The spectral and analytical data for the iodoperfluoroalkylation product, e.g., **2a** is as follows: white solid (obtained as a stereoisomeric mixture); ^1H NMR (300 MHz, $CDCl_3$) [(*E*)-**2a**] δ 1.14 (s, 9H), 3.57 (t, JH-F = 17.5 Hz, 2H), 6.69 (s, 1H). [(*Z*)-**2a**] δ 1.21 (s, 9H), 3.40 (t, JH-F = 17.4 Hz, 2H), 6.21 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) [(*E*)-**2a**] δ 30.37, 38.58, 39.78 (t, JC-F = 20.9 Hz), 78.52, 159.32. [(*Z*)-**2a**] δ 29.29, 34.13, 48.28 (t, JC-F = 20.8 Hz), 78.74, 153.62; IR (NaCl) 3444, 2966, 1645, 1210, 1150, 1110, 889, 649 cm^{-1}; MS (EI), $m/z=742$ (M^+, 23); Anal. calcd for $C_{17}H_{12}F_{21}I$: C, 27.51; H, 1.63. Found: C, 27.36; H, 1.63.

6. (a) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH: Weinheim, 1988; (b) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.
7. The *E*/*Z* ratios of iodoperfluoroalkylated products were determined by the measurement of NOE difference spectra. In the case of (*Z*)-**2a**, for example, irradiation of the vinylic singlet at δ 6.21 resulted in an enhancement of the signal at δ 3.40 (allylic triplet), whereas irradiation of the vinylic singlet of (*E*)-**2a** at δ 6.69 indicated no enhancement of the signal at δ 3.57 (allylic triplet).