



Redox system for perfluoroalkylation of arenes and α -methylstyrene derivatives using titanium oxide as photocatalyst

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ABSTRACT

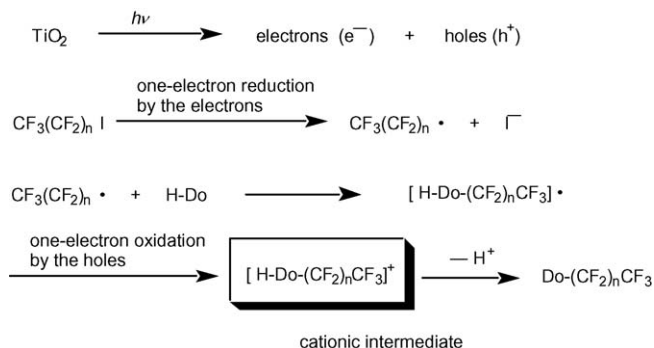
Photoirradiation of titanium oxide (TiO_2) excites the electrons from the valence band to the conduction band, leaving holes in the valence band. Using these holes and electrons, it is possible to perform one-electron oxidations and reductions. We developed a method for the photocatalytic perfluoroalkylation of aromatic rings such as benzene and its derivatives, naphthalene and benzofuran with perfluoroalkyl iodide by the combination of reduction and oxidation reactions with TiO_2 . Perfluoroalkyl iodide was reduced to a perfluoroalkyl radical by the excited electrons in the conduction band of TiO_2 , and the resulting radical reacted with an aromatic ring to form an arenium radical that was successively oxidized to a cation by the holes in the valence band of TiO_2 . Similarly, the photocatalytic reaction of α -methylstyrene with perfluoroalkyl iodide afforded perfluoroalkylated α -methylstyrene, in which the perfluoroalkyl group is on a methyl carbon.

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1. Introduction

Perfluoroalkyl iodide is a well-known source for the introduction of perfluoroalkyl groups into organic molecules. From a perfluoroalkyl iodide, a perfluoroalkyl radical is relatively easy to produce thermally, photochemically or through the use of a radical initiator [1–3]. One-electron reduction of the iodide is an alternative method of producing perfluoroalkyl radical. A method using $\text{Na}_2\text{S}_2\text{O}_4$ developed by Huang and co-workers [4] and a method using SmI_2 [5] are useful for the reduction of the iodide. Furthermore, electrochemical reduction of the iodide to produce perfluoroalkyl radicals has been well investigated [6]. On the other hand, reports of the perfluoroalkylation of organic molecules with the iodide via a perfluoroalkyl cation are scarce due to the high electronegativity of fluorine [7]. Therefore, electrophilic perfluoroalkylation of organic molecules via a radical intermediate is expected to be a useful method for introducing a perfluoroalkyl group into organic molecules [8]. We investigated the perfluoroalkylation of electron-rich compounds (H-Do) with the iodide via a cationic intermediate by a combination of reduction and subsequent oxidation using titanium oxide (TiO_2) as shown in Scheme 1. Recently, the use of TiO_2 as a photocatalyst has received considerable attention [9]. Photoirradiation of TiO_2 excites electrons from the valence band to the conduction band, leaving holes in the valence band. It may be possible to use these electrons

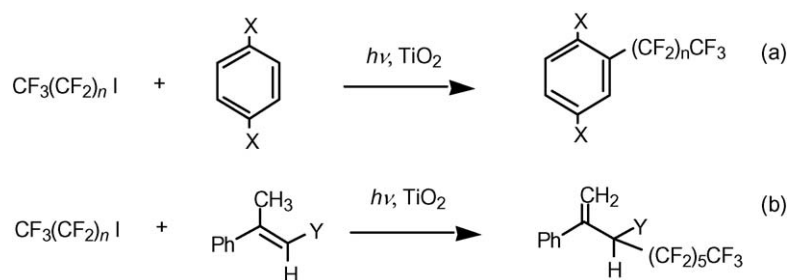
and holes for one-electron reductions and oxidations, respectively. However, studies on the use of TiO_2 as a photocatalyst for carbon–carbon bond formation have been scarcely done [10]; especially no TiO_2 -photocatalytic carbon–carbon bond formation reaction for syntheses of organofluorine compounds has been reported thus far except for our preliminary communication [11]. Here, we report the development of a new redox system using TiO_2 as a photocatalyst to perform perfluoroalkylations that result in carbon–carbon bond formation. The electrons in the conduction band of TiO_2 reduce perfluoroalkyl iodide to form a perfluoroalkyl radical and iodide ion. The resulting radical reacts with an organic molecule to provide a new radical species, which is successively oxidized to the corresponding cationic intermediate as shown in Scheme 1.



Scheme 1.

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Scheme 2.

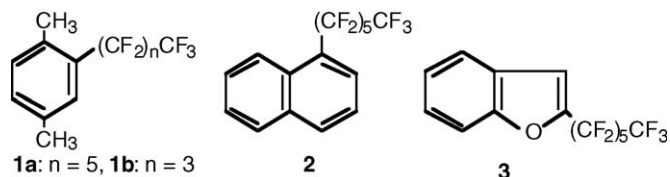
In this paper, we describe the perfluoroalkylation of aromatic rings (Scheme 2(a)), α -methylstyrene (Scheme 2(b)) and their related compounds with perfluoroalkyl iodide under TiO_2 -photocatalytic conditions.

2. Experimental

^1H , ^{13}C , and ^{19}F NMR spectra were acquired with a JEOL JNM-ECA500 (^1H : 500 MHz; ^{13}C : 125 MHz; ^{19}F : 470 MHz) or AL400 (^1H : 400 MHz; ^{13}C : 100 MHz; ^{19}F : 376 MHz) spectrometer in CDCl_3 . Fluorine chemical shifts were determined using PhCF_3 as an internal standard and are given in ppm downfield from an external standard of CF_3COOH (δ_{F} of $\text{PhCF}_3 = 12.6$). Mass spectra were obtained with a Hewlett PACARD 5890 GC/5972 MSD or a JEOL JMS AX-505H spectrometer equipped with a JEOL JMA 5000 mass data system using an electron-impact (EI) ionization technique at 70 eV. HPLC analysis was performed with a Shimadzu SPD-6A liquid chromatograph equipped with a Cosmosil 5C18 (4.6 mm $\times$ 250 mm, Nacalai Tesque, reverse-phase column) with $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (80/20 by volume) as eluent. Perfluorobutyl and perfluorohexyl iodides were obtained from Tokyo Kasei Kogyo Co., Ltd. and purified by distillation over $\text{Na}_2\text{S}_2\text{O}_3$ if necessary. α -Methylstyrene was obtained from Tokyo Kasei Kogyo Co., Ltd. and purified by distillation if necessary. 3,4-Dihydro-1-methylnaphthalene was prepared from 1-methyl-1-hydroxy-1,2,3,4-tetrahydronaphthalene, which was synthesized from α -tetralone (Aldrich Chemicals) via a Grignard reaction. Commercially available aromatic compounds such as *p*-xylene, 1,4-dichlorobenzene, naphthalene and benzofuran were used without further purification. The solvent for the reaction, CH_3CN , was distilled over CaH_2 just prior to use. TiO_2 (ST-01; Ishihara Sangyo Co., Ltd.) was used for all photocatalytic reactions in this study.

2.1. Photocatalytic aromatic perfluoroalkylation with perfluoroalkyl iodide

Perfluoroalkylated *p*-xylene (**1a** and **1b**) [12], naphthalene (**2**) [13,14], and benzofuran (**3**) [15] were prepared by the following procedures.



2.1.1. Perfluoroalkylation of *p*-xylene

TiO_2 (80 mg) was dispersed in CH_3CN (54 mL) and sonicated for 10 min. To the resulting disperse system, CH_3OH (6 mL), NaBF_4 (110 mg), perfluorohexyl iodide (1.114 g, 2.5 mmol) and *p*-xylene (25 mmol) were added. Under a nitrogen atmosphere with stirring

to disperse TiO_2 , the solution was photoirradiated for 64 h using two metal halide lamps (National Sky-beam MT-70) that irradiated the reaction vessel from both sides. During the photoirradiation for 64 h, the color of TiO_2 changed from white to blue gray, and the iodide was consumed completely as determined by HPLC. After removal of TiO_2 by filtration, the solvent and unreacted *p*-xylene were removed by rotary evaporation, and the residue was dissolved in ether (50 mL). The resulting ether solution was washed with 10% aq $\text{Na}_2\text{S}_2\text{O}_3$ (50 mL) and then brine (50 mL), and dried over MgSO_4 . The ether was removed under reduced pressure to give crude **1a**. The crude product was purified by column chromatography on silica gel with hexane as eluent to give **1a** (462 mg, 44% yield based on the iodide, colorless oil) in its pure form.

1a: ^1H NMR (CDCl_3 , δ): 2.36 (s, 3H), 2.43 (brs, 3H), 7.16 (d, $J = 8.0$ Hz, 1H), 7.23 (d, $J = 8.0$ Hz, 1H), 7.30 (s, 1H); ^{19}F NMR (CDCl_3 , δ): -5.04 (3F), -30.00 (2F), -44.62 (2F), -45.48 (2F), -46.60 (2F), -49.84 (2F); MS (m/z): 424 (M^+), 155.

Similarly, **1b** was obtained from the reaction of nonafluorobutyl iodide with *p*-xylene.

1b: ^{19}F NMR (CDCl_3 , δ): -5.73 (3F), -31.18 (2F), -46.52 (2F), -50.83 (2F); MS (m/z): 324 (M^+), 155.

2.1.2. Perfluoroalkylation of naphthalene

Similarly, a solution of perfluorohexyl iodide (1.114 g, 2.5 mmol) and naphthalene (5.0 mmol) was photoirradiated for 30 h under a nitrogen atmosphere with stirring to disperse TiO_2 . The color of the TiO_2 changed from white to blue gray. After 30 h of photoirradiation, about 2.12 mmol of the iodide was consumed as determined by HPLC. After removal of TiO_2 by filtration, the solvent was removed by rotary evaporation, and the residue was dissolved in 50 mL of ether. The resulting ether solution was washed with 10% aq $\text{Na}_2\text{S}_2\text{O}_3$ (50 mL) and then brine (50 mL), and dried over MgSO_4 . The ether was removed under reduced pressure. The residue was purified by column chromatography on silica gel with hexane as eluent to give a mixture of 1-tridecafluorohexylnaphthalene (**2**) and 2-tridecafluorohexylnaphthalene (358 mg, 44% yield based on the consumed iodide, 6/1 mixture as determined by ^{19}F NMR, colorless oil). Unreacted naphthalene was recovered later during the purification by column chromatography.

2: ^1H NMR (CDCl_3 , δ): 7.59 (m, 3H), 7.83 (m, 1H), 7.92 (m, 1H), 8.06 (m, 1H), 8.23 (m, 1H); ^{19}F NMR (CDCl_3 , δ): -5.01 (3F), -28.69 (2F), -44.61 (2F), -45.74 (2F), -46.94 (2F), -50.35 (2F); MS (m/z): 446 (M^+), 177.

2.1.3. Perfluoroalkylation of benzofuran

The reaction of perfluorohexyl iodide (1.114 g, 2.5 mmol) with benzofuran (5.0 mmol) was performed using the same procedure as the perfluoroalkylation of *p*-xylene. After 50 h of photoirradiation, 1.97 mmol of the iodide was consumed as determined by HPLC. After removal of TiO_2 by filtration from the reaction mixture, the solvent was removed by rotary evaporation, and the residue

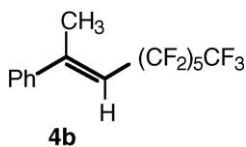
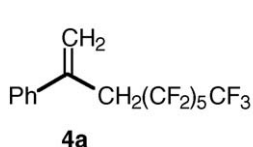
was dissolved in 50 mL of ether. The resulting ether solution was washed with 10% aq $\text{Na}_2\text{S}_2\text{O}_3$ (50 mL) and then brine (50 mL), and dried over MgSO_4 . The ether was removed by rotary evaporation, and then the unreacted benzofuran was removed under reduced pressure using a vacuum pump. The residue was purified by column chromatography on silica gel with hexane as eluent to give **3** (298 mg, 43% yield based on the consumed iodide, colorless oil). In this reaction, almost no regioisomers were produced.

3: ^1H NMR (CDCl_3 , δ): 7.25 (m, 1H), 7.35 (m, 1H), 7.46 (m, 1H), 7.59 (m, 1H), 7.69 (m, 1H); ^{19}F NMR (CDCl_3 , δ): –5.01 (3F), –36.04 (2F), –46.15 (2F), –46.89 (2F), –47.02 (2F), –50.36 (2F); MS (m/z): 436 (M^+), 167.

2.2. Photocatalytic perfluoroalkylation of α -methylstyrene and its derivatives

2.2.1. Reaction with α -methylstyrene

TiO_2 (80 mg) was dispersed in CH_3CN (58 mL) and sonicated for 10 min. To the resulting disperse system, CH_3OH (2 mL), NaBF_4 (110 mg), perfluorohexyl iodide (1.114 g, 2.5 mmol) and α -methylstyrene (600 mg, 5.1 mmol) were added. Under a nitrogen atmosphere with stirring to disperse TiO_2 , the solution was photoirradiated for 45 h using two metal halide lamps (National Sky-beam MT-70) that irradiated the reaction vessel from both sides. The color of the TiO_2 changed from white to blue gray. After 45 h of photoirradiation, 1.92 mmol of the iodide was consumed as determined by HPLC. After removal of the TiO_2 by filtration, the solvent and unreacted α -methylstyrene were removed by rotary evaporation, and the residue was dissolved in 50 mL of ether. The resulting ether solution was washed with 10% aq $\text{Na}_2\text{S}_2\text{O}_3$ (50 mL) and then brine (50 mL), and dried over MgSO_4 . The ether was removed under reduced pressure. The residue was subjected to column chromatography on silica gel with hexane as eluent. 2-Phenyl-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononene (441 mg, 52% yield based on the consumed iodide, colorless oil) was obtained as a mixture of 1-nonene (**4a** [16]) and 2-nonene (**4b** [16]) in the ratio of 13/1 as determined by ^{19}F NMR. The mixture was again subjected to column chromatography on silica gel with hexane as eluent. First, a small amount of **4b** was eluted. Then, the main product **4a** was eluted and obtained in its pure form.



4a: ^1H NMR (CDCl_3 , δ): 3.29 (t, $J_{\text{HF}} = 18$ Hz, 2H), 5.41 (s, 1H), 5.64 (s, 1H), 7.29–7.39 (m, 5H); ^{19}F NMR (CDCl_3 , δ): –5.38 (3F), –36.90 (2F), –46.37 (2F), –47.43 (2F), –47.60 (2F), –50.70 (2F); MS (m/z): 436 (M^+), 167, 117, 115, 103.

4b: ^1H NMR (CDCl_3 , δ): 2.28 (s, 3H), 5.75 (t, $J_{\text{HF}} = 16$ Hz, 1H), 7.29–7.39 (m, 5H); ^{19}F NMR (CDCl_3 , δ): –5.41 (3F), –30.00 (2F), –46.21 (2F), –47.50 (2F), –47.99 (2F), –50.71 (2F); MS (m/z): 436 (M^+), 167, 147, 127.

2.2.2. Reaction with 2-phenyl-2-butene

The reaction of perfluorohexyl iodide (1.114 g, 2.5 mmol) with 2-phenyl-2-butene (660 mg, 5.0 mmol) was performed using the same procedure as the perfluoroalkylation of *p*-xylene. After 22 h of photoirradiation, 1.70 mmol of the iodide was consumed as determined by HPLC. After removal of TiO_2 by filtration from the reaction mixture, the solvent and unreacted 2-phenyl-2-butene were removed by rotary evaporation, and the residue was dissolved in 50 mL of ether. The resulting ether solution was washed with 10% aq $\text{Na}_2\text{S}_2\text{O}_3$ (50 mL) and then brine (50 mL), and

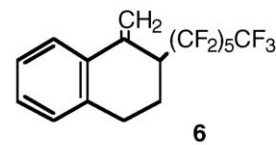
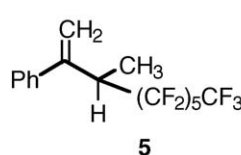
dried over MgSO_4 . The ether was removed under reduced pressure. The residue was purified by column chromatography on silica gel with hexane as eluent, and 3-methyl-2-phenyl-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononene (**5**) (376 mg, 49% yield based on the consumed iodide, colorless oil) was obtained.

5: ^1H NMR (CDCl_3 , δ): 1.46 (d, $J = 5.6$ Hz, 3H), 3.54 (m, 1H), 5.43 (s, 1H), 5.53 (s, 1H), 7.31–7.36 (m, 5H); ^{13}C NMR (CDCl_3 , δ): 15.10, 40.52 (t, $J_{\text{CCF}} = 21.7$ Hz), 117.90, 126.39, 127.75, 128.45, 142.10, 145.24; ^{19}F NMR (CDCl_3 , δ): –5.01 (3F), –37.43 and –40.83 (ABq, $J_{\text{FF}} = 277$ Hz, 2F), –44.04 and –44.20 (ABq, $J_{\text{FF}} = 277$ Hz, 2F), –46.05 (2F), –47.02 (2F), –50.36 (2F); HRMS (m/z): M^+ calcd for $\text{C}_{16}\text{H}_{11}\text{F}_{13}$, 450.0653; found, 450.0632.

2.2.3. Reaction with 3,4-dihydro-1-methylnaphthalene

When the photocatalytic reaction of perfluorohexyl iodide with 3,4-dihydro-1-methylnaphthalene was performed using a procedure similar to that described in the case of the reaction with α -methylstyrene, further reaction occurred between 2-tridecafluorohexyl-1,3,4-trihydro-1-methylenenaphthalene (**6**), which was the initial product of the reaction, and perfluoroalkyl radical. Therefore, the photochemical reaction of 3,4-dihydro-1-methylnaphthalene was performed as follows. TiO_2 (40 mg) was dispersed in CH_3CN (27 mL) and sonicated for 10 min. To the resulting disperse system, CH_3OH (3 mL), NaBF_4 (55 mg), perfluorohexyl iodide (445 g, 1.0 mmol) and 3,4-dihydro-1-methylnaphthalene (432 mg, 3.0 mmol) were added. The solution was similarly photoirradiated for 16 h. The color of the TiO_2 changed from white to blue gray. After 16 h of photoirradiation, about 0.33 mmol of the iodide remained unreacted as determined by HPLC. After removal of TiO_2 by filtration, the solvent was evaporated and the residue was dissolved in 50 mL of ether. The resulting ether solution was washed with 10% aq $\text{Na}_2\text{S}_2\text{O}_3$ (50 mL) and then brine (50 mL), and dried over MgSO_4 . The ether was removed under reduced pressure. From the residue, 2-tridecafluorohexyl-1,3,4-trihydro-1-methylenenaphthalene (**6**) (135 mg, 44% yield based on the consumed iodide, colorless oil) was obtained by column chromatography on silica gel with hexane as an eluent.

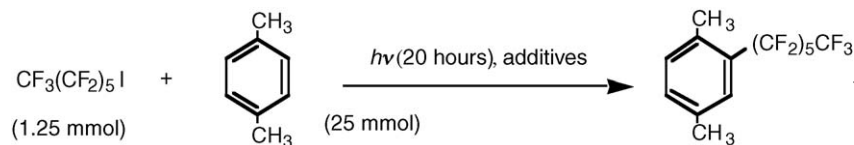
6: ^1H NMR (CDCl_3 , δ): 2.14 (m, 1H), 2.32 (m, 1H), 2.80 (m, 1H), 3.02 (m, 1H), 3.44 (m, 1H), 5.22 (s, 1H), 5.71 (s, 1H), 7.17 (m, 1H), 7.23 (m, 2H), 7.56 (m, 1H); ^{13}C NMR (CDCl_3 , δ): 22.78, 26.13, 43.00 (t, $J_{\text{CCF}} = 20.6$ Hz), 116.41, 124.84, 126.36, 128.08, 128.45, 134.26, 136.14, 147.46; ^{19}F NMR (CDCl_3 , δ): –5.39 (3F), –35.06 and –39.92 (ABq, $J_{\text{FF}} = 278$ Hz, 2F), –44.81 (2F), –46.47 (2F), –47.35 (2F), –50.71 (2F); HRMS (m/z): M^+ calcd for $\text{C}_{17}\text{H}_{11}\text{F}_{13}$, 462.0653; found, 462.0696.



3. Results and discussion

3.1. Photocatalytic aromatic perfluoroalkylation

The photochemical perfluoroalkylation of an aromatic ring with perfluoroalkyl iodide was examined under the various conditions shown in Table 1; the reaction was monitored by HPLC and GC–MS. Under a N_2 atmosphere, a solution of $\text{CF}_3(\text{CF}_2)_5\text{I}$ (1.25 mmol) and *p*-xylene (25 mmol) in 30 mL CH_3CN was irradiated with light having a wavelength of more than 350 nm using a metal halide lamp. However, the reaction was very slow under the conditions, and more than 90% of the iodide remained unreacted after 20 h of

Table 1Photochemical reaction of perfluorohexyl iodide with *p*-xylene in the presence or absence of TiO₂.

Run	Additive	Solvent	Conversion of $\text{CF}_3(\text{CF}_2)_5\text{I}/\%$ ^a	Yield of $\text{Ar}(\text{CF}_2)_5\text{CF}_3/\%$ ^b
1	None	CH ₃ CN (30 mL)	7	Trace
2	TiO ₂ (40 mg)	CH ₃ CN (30 mL)	8	Trace
3	TiO ₂ (40 mg)	CH ₃ CN (27 mL), –CH ₃ OH (3 mL)	44	20 (45)
4	TiO ₂ (40 mg), NaBF ₄ (55 mg)	CH ₃ CN (27 mL), –CH ₃ OH (3 mL)	67	46 (69)
5	TiO ₂ (40 mg), NaBF ₄ (55 mg)	CH ₃ CN (27 mL), –C ₂ H ₅ OH (3 mL)	64	32 (50)
6	TiO ₂ (40 mg), NaBF ₄ (55 mg)	CH ₃ CN (27 mL), –2-PrOH (3 mL)	8	Trace

^a Determined by HPLC.^b Yields were determined by HPLC based on $\text{CF}_3(\text{CF}_2)_5\text{I}$. The yields based on consumed $\text{CF}_3(\text{CF}_2)_5\text{I}$ are shown in parentheses.

photoirradiation as determined by HPLC analysis (Table 1, run 1). Acceleration of the reaction was not observed even when TiO₂ photocatalyst was used in CH₃CN (Table 1, run 2). Interestingly, using a solvent system of CH₃CN (27 mL) and methanol (3 mL) was found to make the reaction proceed smoothly (Table 1, run 3). The addition of NaBF₄ to the solvent system further accelerated the reaction, and 67% of the iodide was consumed in the reaction performed under these conditions (Table 1, run 4). Such an effect of additives is also reported in the case of the TiO₂-catalyzed photooxygenation of 1,1-diarylethenes performed in the presence of MgClO₄ [17]. The products of the reaction were analyzed by GC–MS, and perfluorohexylated *p*-xylene (**1a**) was detected as the main product. The maximum yield (69%) based on the consumption of perfluorohexyl iodide was obtained in run 4 in Table 1. In a solvent system of CH₃CN with ethanol, aromatic perfluoroalkylation giving **1a** proceeded similarly (Table 1, run 5). However, no effect of 2-propanol on the photocatalytic reaction was observed (Table 1, run 6).

Perfluoroalkyl substituted *p*-xylene (**1a**) was obtained cleanly under the conditions in run 4 in Table 1. As the most plausible mechanism for the production of **1a**, we propose that shown in

Scheme 3. Photoirradiation of TiO₂ excites the electrons from the valence band to the conduction band, leaving holes in the valence band (Scheme 3, Eq. (1)). However, these excited electrons did not reduce the iodide as a result of the recombination of the electrons with the holes (Scheme 3, Eq. (1)), which was probably much faster than the reaction with the iodide (Scheme 3, Eq. (2)). In the presence of methanol, the holes are expected to react with methanol (Scheme 3, Eq. (3)) before recombination of the holes with the electrons can occur, and as a result, the excited electrons were able to reduce the iodide to a perfluoroalkyl radical. The resulting perfluoroalkyl radical reacted with *p*-xylene to form an arenium radical, which was successively oxidized to an arenium cation by the holes (Scheme 3, Eq. (4)). Overall, the success of this aromatic perfluoroalkylation depends on the balance of the oxidation–reduction reactions; methanol and NaBF₄ may act as modulators to maintain this balance.

Furthermore, the TiO₂-photocatalytic aromatic perfluoroalkylations of *p*-xylene, benzene and 1,4-dichlorobenzene with perfluoroalkyl iodide were examined in a mixed solvent system of CH₃CN/CH₃OH (9/1 by volume) in the presence of NaBF₄. The

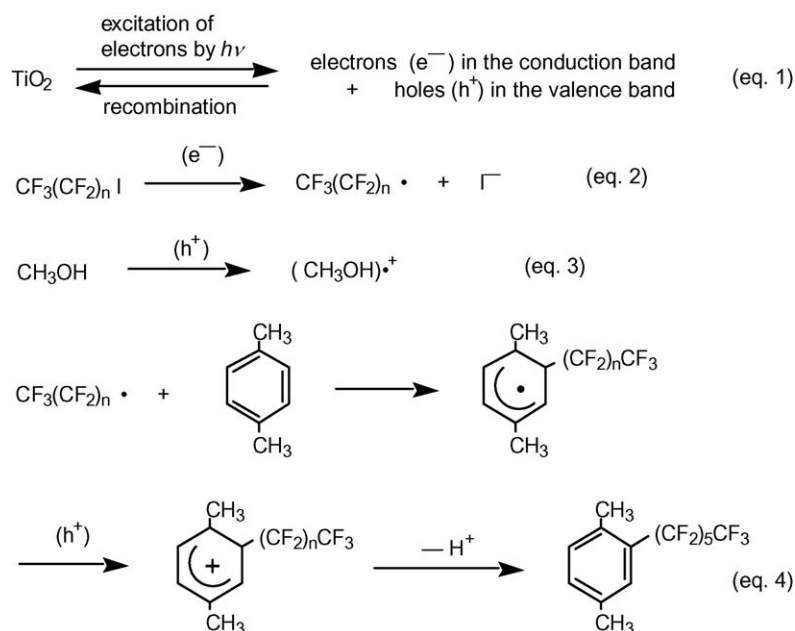
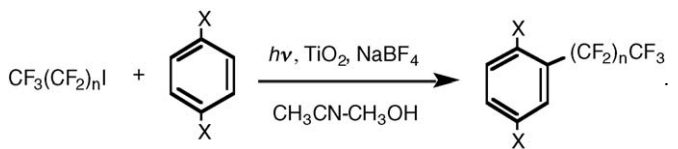
**Scheme 3.**

Table 2
TiO₂-photocatalytic perfluoroalkylations of benzenes.



Run	x of ArH	n of CF ₃ (CF ₂) _n I	Molar ratio, ArH/CF ₃ (CF ₂) _n I	Yield of Ar(CF ₂) _n CF ₃ /%
1	CH ₃	5	2	28
2	CH ₃	5	10	58
3	CH ₃	5	20	72
4	CH ₃	5	30	72
5	CH ₃	3	10	56
6	H	5	10	51
7	Cl	5	10	13

^a Determined by HPLC based on CF₃(CF₂)_nI.

results are shown in Table 2. Photoirradiation was continued until the iodide was almost completely consumed, which required more than 45 h. The photochemical reactions were performed using various molar ratios of *p*-xylene and perfluorohexyl iodide (Table 2, runs 1–4). When the reaction was carried out using 2 mol amt. of *p*-xylene to the iodide, the yield of **1a** was poor (Table 2, run 1). The yield of **1a** was improved to about 70% by using more than 20 mol amt. of *p*-xylene (Table 2, runs 2–4). Similarly, perfluorobutylated *p*-xylene (**1b**) was also obtained in 56% yield (Table 2, run 5). Unfortunately, trifluoromethylation using this protocol with trifluoromethyl iodide was unsuccessful, and almost all of the iodide remained unreacted. The reduction potential of trifluoromethyl iodide is known to be higher than that of perfluorohexyl or butyl iodide [6]. The effectiveness of the TiO₂ photocatalyst as a reducing agent may not be sufficient for the successful reaction of trifluoromethyl iodide using this method. The reaction of perfluorohexyl iodide with benzene or 1,4-dichlorobenzene was also examined (Table 2, runs 6 and 7). Perfluorohexylbenzene was obtained in 51% yield (Table 2, run 6) but the yield of the perfluorohexylated 1,4-dichlorobenzene was poor (Table 2, run 7), even when the reaction was carried out in the presence of 10 mol amt. of 1,4-dichlorobenzene. The reactivity of these arenes in the production of perfluorohexylated arenes was consistent with the electrophilicity of the perfluoroalkyl radical

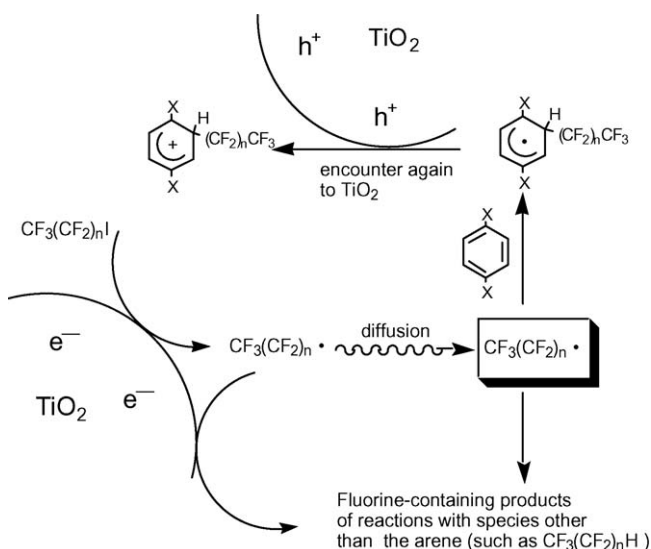
[14,18]. When perfluorohexyl iodide (1.25 mmol) was reacted with a mixture of *p*-xylene (12.5 mmol), benzene (12.5 mmol) and 1,4-dichlorobenzene (12.5 mmol), the molar ratio between the produced arenes (X = CH₃/H) was 1.7/1.0. Almost no perfluorohexylated 1,4-dichlorobenzene was obtained in this reaction.

These results can be explained as follows. There are two possible reaction pathways for the intermediate perfluoroalkyl radical (Scheme 4). The first route is the reaction of the radical on the surface of TiO₂. The other route is the diffusion of the radical into the solvent and subsequent reaction with an arene to produce a perfluoroalkylated arenium radical. The arenium radical in the bulk solution encounters again to TiO₂ to be oxidized by the holes in the TiO₂. Based on the maximum yield obtained for the reaction of *p*-xylene, at least 70% of the perfluoroalkyl radical should diffuse from the surface of TiO₂. In the case of electron-deficient 1,4-dichlorobenzene, the electrophilic perfluoroalkyl radical after diffusion into solution may react with something beside the arene to produce fluorine-containing side products before it reacts with the arene. Thus, the yield of the perfluoroalkylation in 1,4-dichlorobenzene is expected to be low. Only CF₃(CF₂)₅H was characterized among the fluorine-containing side products by ¹⁹F NMR analysis of the solution for the reaction, which showed the characteristic doublet signal of CF₂–H coupling.

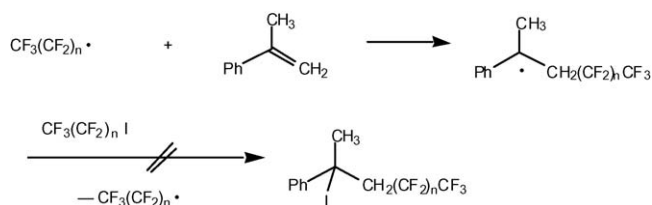
This methodology was applied to the practical preparation of perfluoroalkylated arenes such as *p*-xylene, naphthalene and benzofuran as described in Section 2, and these arenes were obtained in moderate isolated yields. The reactivity of perfluoroalkyl radical with naphthalene is much higher than even that with electron-rich benzenes such as toluene or anisole [14]. Therefore, in the perfluoroalkylation of naphthalene, 2 mol amt. of naphthalene was sufficient to effectively trap the diffusing perfluoroalkyl radical. Similarly, perfluoroalkylation of benzofuran proceeded effectively for the reaction of the iodide with 2 mol amt. of benzofuran. In these reactions, the desired perfluoroalkylated products were easily separated from the starting arenes. Thus, TiO₂-photocatalytic reactions of perfluoroalkyl iodide with electron-rich aromatic compound are proposed as a practical method for introducing perfluoroalkyl groups to the aromatic ring.

3.2. Preparation of perfluoroalkylated α -methylstyrene on the methyl carbon

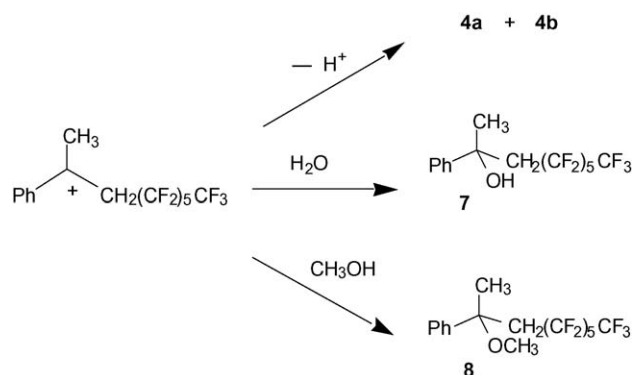
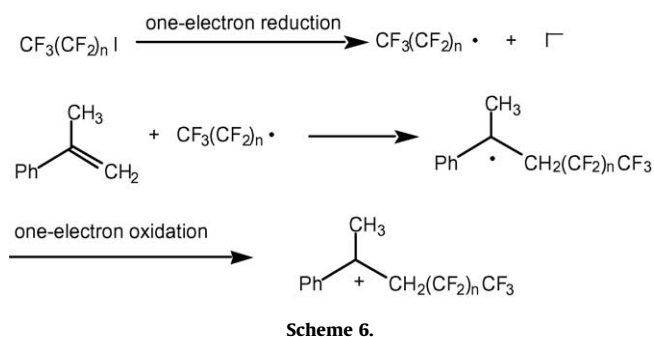
This methodology for reduction and successive oxidation was further investigated in regards to the practical preparation of perfluoroalkylated α -methylstyrene, in which the perfluoroalkyl group is on the methyl carbon, as shown in Scheme 2(b). Free-radical chain iodoperfluoroalkylation of olefins using a perfluoroalkyl iodide is the most important method for the introduction of perfluoroalkyl groups into organic molecules [1–3]. Triethylborane is a superior radical initiator for iodoperfluoroalkylation [19]. However, in the reaction with α -methylstyrene, the produced benzyl-type radical is very stable against iodine abstraction from the perfluoroalkyl iodide and the iodoperfluoroalkylation does not proceed (Scheme 5) [13,20,21]. We have been investigating ways



Scheme 4.



Scheme 5.



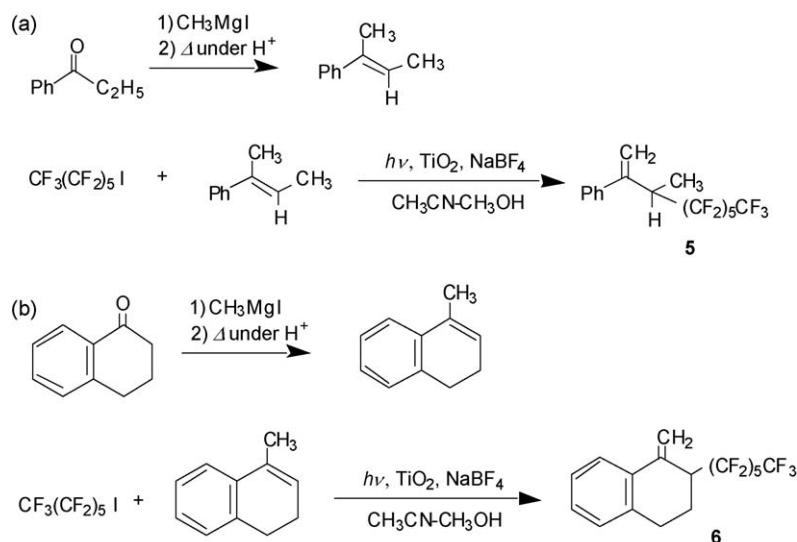
for the produced benzyl-type radical to undergo further reaction for the preparation of fluoroalkylated compounds [13,21], and found a new way to convert the radical to a cation (Scheme 6). The system consists of three steps: one-electron reduction of perfluoroalkyl iodide, the addition of the radical to the olefin and one-electron oxidation of the produced benzyl-type radical to the cation. The reduction and oxidation were carried out by the excited electrons and the holes produced in the TiO_2 photocatalyst.

A solution of perfluoroalkyl iodide and α -methylstyrene in CH_3CN in a dispersion of TiO_2 was photoirradiated under conditions similar to those for the aromatic perfluoroalkylations shown in Table 1. As was reported in our preliminary communication, perfluoroalkylated olefins (**4a** and **4b**), the alcohol **7**, the methoxylated compound **8** and other miscellaneous fluoroalkylated products were detected by GC–MS analysis [11]. These products are thought to be produced via the cationic intermediate, which can likely provide access to various organofluorine compounds (Scheme 7). Interestingly, olefin **4a** was produced preferentially over **4b** from the cation, although this result was inconsistent with the Saytzeff orientation.

In this paper, we focused on the practical preparation of olefin **4a** and related olefins that have high potential as building blocks for the synthesis of fluorine compounds and as starting materials for new types of polymers. Through the use of this reaction with β -substituted α -methylstyrene, namely, 2-phenyl-2-butene synthesized from ethyl phenyl ketone, perfluorohexylated 2-phenyl-1-alkene **5** was prepared in moderate yield (see Scheme 8(a) and Section 2). The various 2-aryl-2-alkenes used as substrates for this reaction are synthesized via the reaction of the corresponding

commercially available ketones and methyl magnesium iodide. Thus, this reaction is expected to be a useful method for the practical preparation of novel fluorinated 2-aryl-1-alkenes. To demonstrate the usefulness of this technique, we prepared fluoroalkylated ring compound (**6**) from α -tetralone (see Scheme 8(b) and Section 2).

Here, we have demonstrated a new system using TiO_2 as a photocatalyst to produce perfluoroalkyl radical that results in perfluoroalkylation of aromatic rings and α -methylstyrene derivatives. Among the various examples for perfluoroalkylation with perfluoroalkyl iodide [3–5,14,19 and the references cited therein], the methodology described here has an important feature to lead to substantial substitution reaction on organic molecule by fluoroalkyl group. In the reactions with aromatic rings, rearomatization of the arenium radicals proceeded effectively, and fluoroalkylated aromatic compounds were obtained as clean products. In the reactions with α -methylstyrene derivatives, the usual addition products of perfluoroalkyl group with iodine and hydrogen atoms to the double bond were not obtained, but fluoroalkyl substituted terminal alkenes were obtained as main products. These are, in our opinions, due to efficient oxidation of the intermediate fluoroalkylated radicals to the corresponding cations by the holes in TiO_2 . Further, TiO_2 is cheap, easy to handle, and non-toxic. Thus, this redox system using TiO_2 is expected to be practical methodology for introducing perfluoroalkyl group to organic molecules.



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