



Photoinduced double perfluoroalkylation of methylacenes



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ABSTRACT

Novel photoinduced double perfluoroalkylation of methylacenes has been described. The reaction proceeded with appropriately substituted methylacenes to produce a mixture of the expected aromatic compounds with Rf groups both at the methyl and its *para* position as well as the corresponding nonaromatic tautomers. Steric repulsive interaction of fluorine atoms in perfluoroalkyl groups with hydrogen atoms at the *peri* positions would be the most significant factor for control of ratios of these products.

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Introduction

Organofluorine compounds have attracted considerable interest due to the high electronegativity and small size of this unique atom.¹ In recent years, aromatic compounds with a perfluoroalkyl containing methylene group ($-\text{CH}_2\text{C}_n\text{F}_{2n+1}$) have found an increasing number of applications in the fields of medicinal chemistry, biochemistry, and functional materials. In particular, because the character as organic semiconductor materials is expected for polycyclic aromatics, exploration of efficient methods is desired for their synthesis. Among them, several studies have already been reported like cross-coupling reactions of benzyl halides with TMSCF_3 ² or aromatic boronic acids with $\text{CF}_3\text{CH}_2\text{I}$.³ A few examples of direct benzylic C–H trifluoromethylation using electrophilic Togni's reagents have also been appeared,⁴ while this reaction was limited to the benzylic C–H bond at the *para* position of 2,4,6-trimethylphenol derivatives. In addition, there is no instance on incorporation of longer perfluoroalkyl chains to benzylic position.

We have previously demonstrated a series of photoinduced radical perfluoroalkylation of olefins and found that perfluoroalkyl iodides smoothly reacted with various kinds of olefins in the presence of aqueous $\text{Na}_2\text{S}_2\text{O}_3$.⁵ Furthermore, the photoinduced radical perfluoroalkylation of anthracenes was found to give perfluoroalkylated-dimerized products.⁶ In the course of our continuing

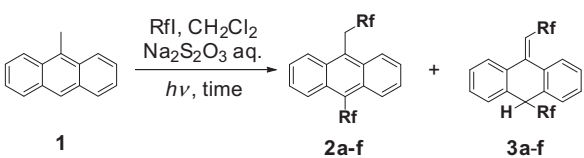
studies, we applied our photoinduced methods to 9-methylanthracene on the basis of the idea that highly reactive benzylic positions for nucleophilic radical reaction⁷ would readily accept perfluoroalkyl radicals. Here we described the novel photoinduced double perfluoroalkylation of methylacenes both at the benzylic and *para* positions.

Results and discussion

At first, we investigated the reaction of 9-methylanthracene with 1.0 equiv of perfluorohexyl iodide in CH_2Cl_2 under UV irradiation in the presence of aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (Table 1, entry 1). As a result, 9-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-10-(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)anthracene (**2a**) with two perfluorohexyl groups both at the benzylic and 10-positions was obtained in 42% yield. At the same time, 9-methylene-9,10-dihydroanthracene type product **3a**, which is the tautomeric form of **2a**, was obtained in 5% yield. The fact that two Rf groups were incorporated at the same time led to utilization of 2.0 equiv of perfluorohexyl iodide to attain 80% yield of the desired **2a** and 10% yield of **3a** (Table 1, entry 2). This process was successfully applied to such a variety of perfluoroalkyl iodides as $^{18}\text{C}_8\text{F}_{17}\text{I}$ and $^{18}\text{C}_{10}\text{F}_{21}\text{I}$ with longer chains as well as $^{13}\text{C}_3\text{F}_7\text{I}$, $^i\text{C}_3\text{F}_7\text{I}$, and CF_3I with shorter or branched chains to give the corresponding products **2** and **3** in good to high yields (Table 1, entries 3–8). In the case of CF_3I , yields of **2e** and **3e** were only 26% and 2%, respectively, because usage of an excess amount of gaseous trifluoromethyl iodide resulted in formation of a complex mixture. It is interesting to note that sterically

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Table 1
Perfluoroalkylation of 9-methylanthracene^a


Entry	Rf	Isolated yield (%)	
		2	3
1 ^b	ⁿ C ₆ F ₁₃ I	41 (a)	5 (a)
2	ⁿ C ₆ F ₁₃ I	80 (a)	10 (a)
3	ⁿ C ₈ F ₁₇ I	70 (b)	8 (b)
4	ⁿ C ₁₀ F ₂₁ I	61 (c)	8 (c)
5	ⁿ C ₃ F ₇ I	66 (d)	8 (d)
6	CF ₃ I	26 (e)	2 (e)
7	ⁱ C ₃ F ₇ I	—	87 (f)
8 ^c	ⁱ C ₃ F ₇ I	—	62 (f)

^a Reaction conditions: 9-methylanthracene (0.24 mmol), RfI (0.48 mmol), Na₂S₂O₃ (1.2 mmol), and water (1.0 mL) in CH₂Cl₂ (5.0 mL) under UV irradiation for 6 h.

^b 1.0 equiv of C₆F₁₃I was employed.

^c Reaction for 1 h.

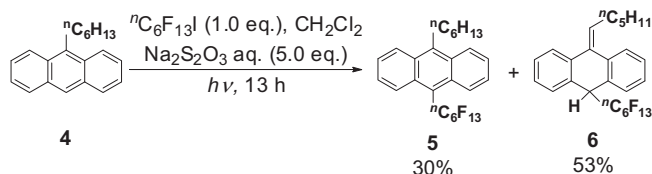
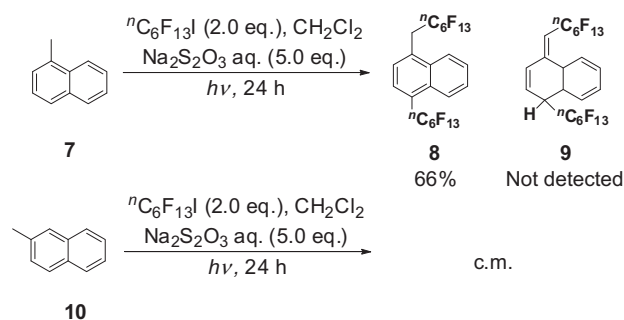
bulkier perfluoroisopropyl iodide did not furnish the compound **2f** but instead **3f** in high yield (Table 1, entry 7). This preference for **3f** would be due to the different steric requirement of ⁱC₃F₇I from other linear RfI employed, and was actually not time-dependent because shorter reaction time as shown in entry 8 afforded the same **3f** specificity in spite of partial decrease of its yield.

In the case of 9-hexylanthracene **4**, perfluoroalkylation occurred only at the 10 position to furnish tautomeric mixtures of **5** and **6** in 30% and 53% yields, respectively (Scheme 1). The results show the importance of the methyl group for double perfluoroalkylation.

Our next interest was focused on the perfluoroalkylation of 1- and 2-methylnaphthalenes (**7** and **10**) (Scheme 2). Although it took longer time, double perfluoroalkylated adduct **8** was specifically constructed from **7** in 66% yield with recovery of the starting material (30%) and without any detection of the corresponding tautomer **9**. On the other hand, the reaction with the isomeric 2-methylnaphthalene **10**, which is blocked at the *para* position of the methyl group, gave complex mixture including starting material.

We also investigated the possible usage of 6-methylpentacene (**11**) as the substrate (Scheme 3). Different from the cases stated above, it is quite interesting to note that this reaction specifically provided the dearomatized exomethylene type product **13** in 63% yield without any trace formation of its aromatized tautomer **12**.

The proposed mechanism for the formation of doubly perfluoroalkylated anthracenes **2** is described in Scheme 4. If benzyl radical is generated before the attack of the perfluoroalkyl radical (Path A), the former radical would react with perfluoroalkyl iodide to give the compound **A**. Following entry of the perfluoroalkyl radical at the *para* position to the original methyl group produced the intermediate **C**. However, if the illumination allowed to prepare the perfluoroalkyl radical preferentially, this species would

**Scheme 1.** Perfluoroalkylation of 9-hexylanthracene.**Scheme 2.** Perfluoroalkylation of methylnaphthalenes.

construct a new bond at the 10 position of anthracene **1** to form the exomethylene type intermediate **B** (Path B). Incorporation of the second perfluoroalkyl radical to the methylene terminal should afford the same radical intermediate **C**. Following one electron transfer from **C** to RfI,⁸ release of the proton attached to the ring or at the benzylic position resulted in production of the rearomatized product **2** or the methylene type compound **3**, respectively. Moreover, with reference to the previous computational work,^{9e} the exomethylene form **14** in an equilibrating relationship with **1** would be the alternative substrate to get access to **2** and/or **3**. Thus, formation of **2** was explained by generation of a radical at the original 10 position which was further reacted with RfI.

For confirmation of the intermediates produced, the reaction mixture was periodically checked by ¹H NMR in every one hour, while neither compound **A** nor **B** was observed. When the reaction followed Path A, the initially formed Rf radical should capture the H radical from the methyl group at the 9 position. However, the fact that the characteristic NMR peak of RfH was not detected at all led to denial of the possibility of this route, and thus, we considered the Path B more probable.

Besides, we were intriguing about formation of dearomatized products **3** and **13**. In 1949, 6,13-dihydro-6-methylenepentacene has been reported in a tautomeric relationship with 6-methylpentacene with the higher abundance of the former.^{9a} Several articles have disclosed on such tautomerization and bimolecular hydrogen transfer mechanism was suggested.⁹ For clarification of the driving force of the tautomerization of anthracene derivatives, **2a** was irradiated in dichloromethane with high pressure lamp, which did not affect any isomerization to the tautomer **3a** but formation of the [4+4] photodimer **14** (Scheme 5). Furthermore, **2a** was proved to be decomposed by heating to 220 °C. Thus, it was concluded that tautomerization of **2a** to **3a** was not occurred at least under these conditions.

For obtaining information from the energetic point of view, computation has been performed by Gaussian 09W¹⁰ using the B3LYP/6-31+G* level of theory for comparison between anthracenes **2** and the corresponding exomethylene type materials **3** with both linear and branched C₃F₇ substituents, thus for **2d**, **2f**, **3d**, and **3f** (Fig. 1). The obtained energies for these compounds showed interesting tendencies that **2d** with the linear C₃F₇ group was found to be more stable than **3d** by 4.2 kcal/mol while the totally opposite trend was noticed for compounds with the (CF₃)₂CF moiety where **3f** was more favorable to **2f** by 2.0 kcal/mol.

The anthracene type compounds **2** usually suffered from the steric repulsive interaction between Rf groups and hydrogen atoms at the *peri* positions which seems to affect the angles of C¹–C¹⁰–C⁹ and C⁴–C⁵–C⁶ of 176.8° and 171.8° for **2d**, and 171.1° and 164.3° for **2f**, respectively (Table 2). At the same instance, the dihedral angles of C^{4a}–C^{10a}–C¹⁰–C¹¹ and C^{10a}–C^{4a}–C⁵–CF₂ were obtained as 174.6° and 171.3° for **2d**, and 176.9° and 162.3° for **2f**, respectively. It is quite clear that deviation of these angles from the ideal values of

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