Perfluorooctylation of aromatic compounds with perfluoroazooctane upon 185 nm irradiation in a two-phase system

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An efficient method for the preparation of perfluorooctylated aromatic and heteroaromatic compounds has been developed using photolysis of perfluoroazooctane (*E*)-1 upon 185 nm irradiation. The use of a two-phase system made up of a perfluorohexane solution of (*E*)-1 and a suitable aromatic compound has proved efficient for this reaction. The photolytic mechanism of (*E*)-1 upon 185 nm irradiation has also been investigated on the basis of quantum yield, light intensity dependence and UV–VIS spectra. It is shown that (*E*)-1 is photoisomerized by one photon absorption to the (*Z*)-isomer, with subsequent extrusion of nitrogen by a second photon absorption.

Introduction

Perfluoroalkyl-containing organic compounds have attracted much attention in the field of medicinal chemistry and material science because of their unique properties, due to the presence of fluorine atoms, namely biological activity and water/oil repellent properties.[1] Thermal- and photo-induced perfluoroalkyl radicals have been used in organofluorine chemistry to introduce perfluoroalkyl groups into organic compounds.[2] The photochemical generation of perfluoroalkyl radicals from perfluoroalkyl halides, perfluoroalkanesulfonyl chlorides, and perfluoroalkylmetallic reagents have been reported by many workers to date.[2]

The photochemistry of azo compounds has been extensively investigated in the field of organic chemistry.[3] It is well known that azoalkanes are photolyzed to give carbon-centered radicals upon UV irradiation, accompanied by extrusion of nitrogen which is inert to the reaction system.[4] Few reports on perfluoroalkylation of organic compounds by photolysis of perfluoroalkylazo compounds have been published,[5] though they are potentially useful for the photochemical formation of perfluoroalkyl radicals.

In this work we report a novel perfluorooctylation of aromatic and heteroaromatic compounds by photolysis of perfluoroazooctane [(*E*)-1] and its photolytic mechanism upon 185 nm irradiation.

Results and discussion

Perfluoroazooctane [(*E*)-**1**] was prepared according to procedures in the literature.[6] The UV–VIS spectrum of (*E*)-**1** in hexane is shown in Fig. 1, indicating that the azo group of (*E*)-**1** absorbs light at λ_{max} 188 nm (π–π*) and λ_{max} 380 nm (n–π*). As the π–π* absorption of (*E*)-**1** has a much more intense molar extinction coefficient (ε 23 100 l mol^{-1} cm^{-1}) than the n–π* absorption (ε 30), it was expected that vacuum ultraviolet irradiation would lead an effective denitrogenation of (*E*)-**1**.[7]

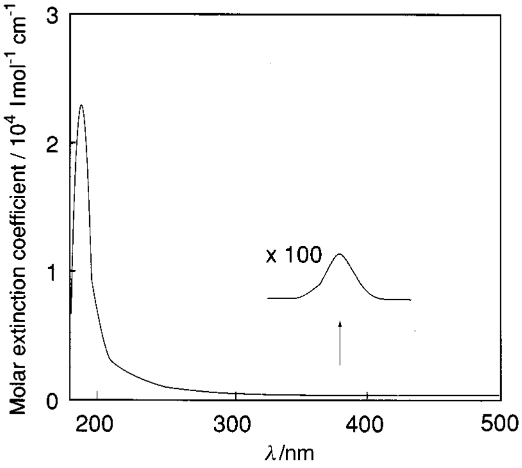
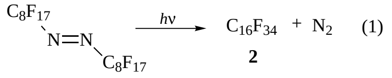


Fig. 1 UV–VIS spectrum of (*E*)-**1** in hexane

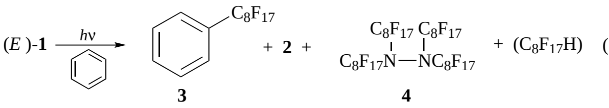
A hexane solution of (*E*)-**1** (1 × 10^{-3} mol l^{-1}) was irradiated at >300 nm light with a high pressure mercury lamp for 24 h. It was shown by GC–MS and UV–VIS analyses of this reaction mixture that the photolysis of (*E*)-**1** by extrusion of nitrogen was negligible, and that *trans–cis* isomerization of **1** was the main reaction occurring during the irradiation. On the other hand, decomposition of (*E*)-**1** was effected completely with the use of 185 nm light from a low pressure mercury lamp for 7 h to give perfluorohexadecane (**2**) from the recombination of perfluorooctyl radicals [reaction (1)].[8] These results indicate that



(*E*)-**1**

185 nm irradiation (π–π* excitation) is much more effective for the denitrogenation of (*E*)-**1** than >300 nm irradiation (n–π* excitation).[7] Adam *et al.* also reported that cyclic azoalkanes decomposed to generate alkyl radicals upon 185 nm irradiation (π–π* excitation), whereas they were slow to extrude nitrogen upon > 300 nm irradiation (n–π* excitation).[9]

An attempt was made to introduce a perfluorooctyl radical into benzene by 185 nm photolysis of (*E*)-**1**. Benzene solutions of (*E*)-**1** (1 × 10^{-3} mol l^{-1}) were irradiated with 185 nm light under a nitrogen atmosphere at room temperature [reaction (2)]. The time-course results of this photoreaction, monitored by GC–MS with nonane and undecane as internal standards, are shown in Fig. 2. After irradiation of the benzene solution for 7 h, the desired perfluorooctylbenzene[10] (**3**) was obtained in



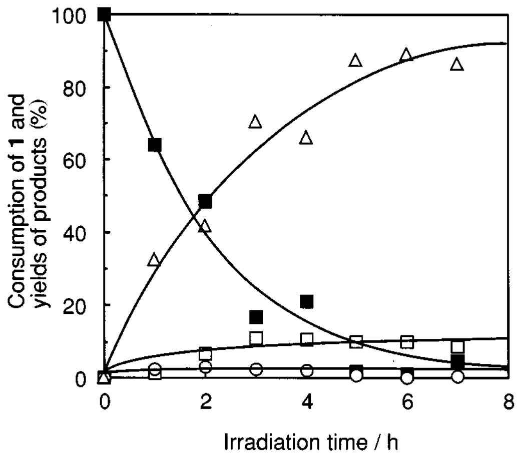


Fig. 2 Photolysis of (*E*)-**1** in benzene with a low pressure mercury lamp. ■, **1**; ○, **2**; □, **3**; △, **4**.

13% yield, together with **2** in 1% yield. It is assumed that the low yield of **3** is due to the formation of tetrakis(perfluorooctyl)hydrazine[8] (**4**) by the reaction of remaining (*E*)-**1** with perfluorooctyl radicals, which are present in low concentration[5] due to the absorption of most of the photons by benzene in this reaction.[11]

In order to improve the efficiency of the generation of perfluorooctyl radicals, we needed to find solvents which have no absorption of 185 nm light and are relatively unreactive towards the resulting radicals. Recently the use of perfluorohexane as an inert reaction medium has been reported for organic reactions.[12] Additionally, perfluoroalkanes have absorption bands in vacuum ultraviolet region (<160 nm) and are easy to remove from the reaction mixture *in vacuo* after irradiation.[13] Therefore, perfluorohexane was selected as a suitable solvent for our purposes. Since hydrocarbon compounds are generally insoluble in perfluorohexane, a two-phase system, consisting of benzene, the substrate, as the upper phase and a perfluorohexane solution of (*E*)-**1** as the lower phase, was adopted for this reaction. In general, two-phase systems, consisting of two immiscible solvents, play an important role in organic syntheses[14] and extraction chemistry.[15]

Table 1 Preparation of perfluorooctyl aromatic and heteroaromatic compounds with (*E*)-**1** in two-phase system upon irradiation

Product	Yield (%)[a]
3	70
5	66[b]
6	74[c]
7	52[d]
8	75
9	70
10	65

[a] Yields of this photoreaction are not optimized. [b] Isomer distribution: *o*-, 33%; *m*-, 35%; *p*-, 32%. [c] Isomer distribution: *o*-, 40%; *m*-, 23%; *p*-, 37%. [d] Isomer distribution: *o*-, 42%; *m*-, 25%; *p*-, 33%.

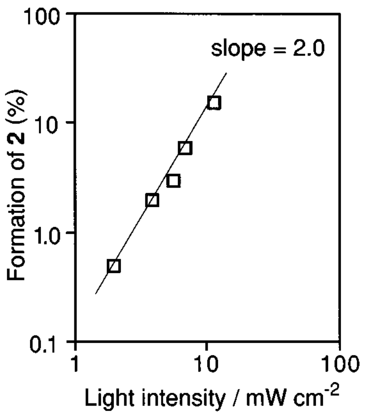
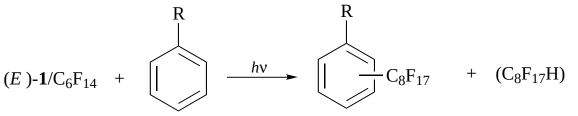


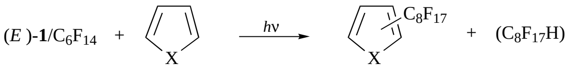
Fig. 3 Light intensity dependence of the formation of **2** by photolysis of (*E*)-**1** upon 185 nm irradiation

A two-phase system, consisting of a perfluorohexane solution of (*E*)-**1** (1×10^{-3} mol l^{-1}) and benzene was prepared. Only the perfluorohexane phase was irradiated with a low pressure mercury lamp at room temperature under a nitrogen atmosphere. After irradiation for 2 h, the two-phase system was converted to a homogeneous solution by the addition of 1,1,2-trichloro-1,2,2-trifluoroethane. It was shown that perfluorooctylbenzene (**3**) was obtained in 70% yield as a desired product by GC–MS analysis of the solution with *n*-nonane as an internal standard [reaction (3)]. This result indicates that the use of two-phase system for perfluorooctylation of benzene has improved the reaction efficiency. The reaction mechanism for the two-phase system was estimated on the basis of GC–MS and UV–VIS analyses before and after irradiation. Before irradiation it was shown that the upper phase (benzene) did not contain (*E*)-**1** at all and that the lower phase contained a small amount of benzene (*ca.* 10^{-4} mol l^{-1}). After irradiation the product **3** was obtained in a ratio of 4 : 1 from the perfluorohexane and benzene phases, respectively. From these results it seems likely that photolysis of (*E*)-**1** occurred in the perfluorohexane phase generating the perfluorooctyl radical, which reacted with the small amount of benzene dissolved in the perfluorohexane phase or at the interface of the two phases to give **3**. This reaction system takes advantage of an efficient generation of perfluorooctyl radicals in the lower phase for a shorter irradiation time, compared with photolysis of (*E*)-**1** in benzene, and of a continuous supply of benzene from the upper phase to perfluorooctyl radicals in the lower phase. To investigate the scope and limitation of this method, various benzene derivatives and heteroaromatic compounds were examined as substrates in a similar manner to that described above [reactions (3) and (4)]. As shown in Table 1, perfluorooctylated aromatic compounds **3**, **5**–**10** were obtained in moderate to good yields. These results suggest that this two-phase method is generally applicable to the preparation of perfluoroalkyl aromatic compounds.



(3)

3 R = H
5 R = Me
6 R = OMe
7 R = Cl



(4)

8 X = O
9 X = S
10 X = NH

In order to investigate the photolytic mechanism of (*E*)-**1** upon 185 nm irradiation, the quantum yield and the light intensity dependence of the formation of **2** by photolysis of (*E*)-**1** were examined in perfluorohexane (1×10^{-3} mol l^{-1}). The azo compound (*E*)-**1** was photodenitrogenated upon 185 nm irradiation in a quantum yield ($\Phi_{-azo} = 0.15$)[16] based upon *cis–trans* isomerization of *cis*-cyclooctene ($\Phi_{cis\text{–}trans} = 0.32$) as an actinometer.[7] As shown in Fig. 3, the formation of **2** was proportional to the square of 185 nm light intensity. These results suggest that (*E*)-**1** was photolyzed upon 185 nm irradiation by two-photon absorption in perfluorohexane.[17] This consideration is

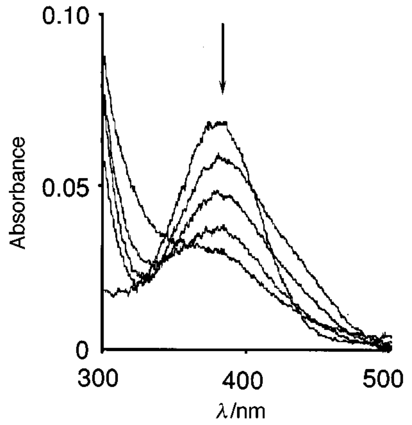
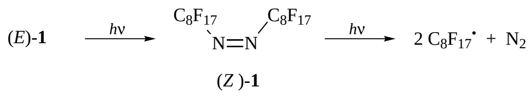


Fig. 4 UV–VIS spectra after 0, 5, 10, 15 and 20 min upon 185 nm irradiation of (*E*)-**1**

consistent with Kaupp and Sauerland's report that high intensity irradiation with a XeCl excimer laser (308 nm) gave a high concentration of pentafluoroethyl radicals by two photon absorption of perfluoroazoethane during the pulse.[11]

In addition, UV–VIS spectral analysis of this photoreaction at 5 min intervals indicated that the intensity of the absorption band of azo group at 380 nm decreased with increase of irradiation time and that a broad absorption band which appeared at longer wavelength decreased gradually (Fig. 4). The azo group of (*E*)-**1** has an absorption band at λ_{max} 380 nm, whereas that of (*Z*)-**1** absorbs at λ_{max} 435 nm.[11] These spectral changes indicate that *trans–cis* isomerization of (*E*)-**1** and the subsequent denitrogenation of resulting (*Z*)-**1** took place during the irradiation. In order to confirm the speculated mechanism of this two-photon process it was necessary to investigate the light intensity dependence of the photolysis of pure (*Z*)-**1** upon 185 nm irradiation. However, as it was difficult to obtain pure (*Z*)-**1** from the direct preparation and isomerization of (*E*)-**1**, (*Z*)-rich **1** was used (*trans*:*cis* = 1.00:1.46), which was obtained from photoisomerization of (*E*)-**1** in cyclohexane (5×10^{-3} mol l^{-1}) upon 370 nm irradiation with Xe lamp through filters for 2 h at room temperature.[11] As shown in Fig. 5, the slope of the formation of **2** against various light intensities was 1.4, showing that this photolysis of (*Z*)-rich **1** consisted of the mixture of one- and two-photonic processes. These results suggest that (*E*)-**1** is photoisomerized to (*Z*)-**1** by one photon absorption,[7] followed by photodecomposition of (*Z*)-**1** to perfluorooctyl radicals by another photon absorption (Scheme 1).



Scheme 1

In conclusion, an efficient method for the preparation of perfluorooctylated aromatic compounds was developed using photolyis of (*E*)-**1** upon 185 nm irradiation. The use of a two-phase system containing a perfluorohexane solution of (*E*)-**1** and aromatic compounds was useful for the efficient generation of perfluorooctyl radicals and subsequent perfluorooctylation of aromatic compounds. It was found that photolysis of (*E*)-**1** took place *via trans–cis* isomerization and denitrogenation of (*Z*)-**1** *via* a two-photon process.

Experimental

All photolyses and isomerization were carried out in quartz cuvettes at room temperature. The light sources were a 60 W low pressure mercury lamp (Eikosha EL-S-SQ-60) for 185 nm irradiation without any filters unless otherwise noted. In the case of only 185 nm irradiation a 185 nm bandpass filter (185 nm transmission 17.2%, Acton Research Corp. 185-HR-25) was employed with the lamp described above. For >300 nm irradiation a 500 W high pressure mercury lamp (Ushio USH-500D) through a filter (Toshiba UV-31) and for 370 nm irradiation a 500 W Xe lamp (Ushio UI-501C) through filters (Toshiba UV-35 and UV-D33S filter) were used. UV–VIS spectra were measured on a Shimadzu UV-265. ^{19}F NMR spectra were recorded on a Varian Gemini 300BB and mass spectra on a Shimadzu GCMS-QP1000EX.

Benzene and toluene, spectroscopy grade from Merck KGaA, perfluorohexane from PCR INCORPORATED, and *cis*-cyclooctene from Merck KGaA were used without purification. Anisole, chlorobenzene, furan, thiophene and pyrrole from Tokyo Chemical Industry Co., Ltd. were purified by distillation before use.

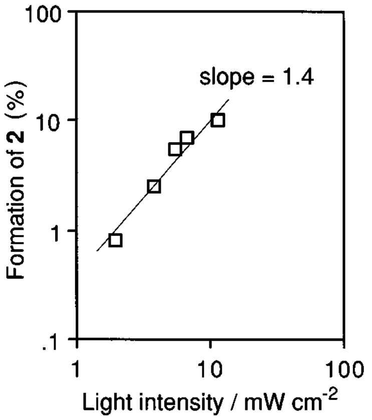


Fig. 5 Light intensity dependence of the formation of **2** by photolysis of (*Z*)-rich **1** upon 185 nm irradiation

Photolysis of (*E*)-1 in benzene

A benzene solution of (*E*)-**1** (1×10^{-3} mol l^{-1}; 3 ml) under a nitrogen atmosphere was irradiated with a low pressure mercury lamp for 7 h or with a high pressure mercury lamp for 24 h. The reaction mixture was analyzed by GC–MS with internal standards (*n*-nonane and *n*-undecane).

Photolysis of (*E*)-1 in two-phase system

A perfluorohexane solution of (*E*)-**1** (1×10^{-3} mol l^{-1}; 2 ml) and aromatic compounds (1 ml) were prepared under a nitrogen atmosphere. After only the perfluorohexane phase had been irradiated with a low pressure mercury lamp for 2 h, 1,1,2-trichloro-1,2,2-trifluoroethane (1 ml) was added in the vessel, and then the homogeneous solution was analyzed by GC–MS. The products were characterized by co-injection of authentic samples prepared according to literature procedures[18] on a GC–MS.

Determination of 185 nm photolysis quantum yield of (*E*)-1

A degassed perfluorohexane solution of (*E*)-**1** (1.01×10^{-3} mol l^{-1}; 3 ml) were irradiated with a low pressure mercury lamp (1 cm^2) equipped with a 185 nm bandpass filter for 5 min. A perfluorohexane solution of *cis*-cyclooctene (2.48×10^{-4} mol l^{-1}; 3 ml) were irradiated for an actinometer ($\Phi_{cis-trans} = 0.32$) in a similar manner as mentioned above. The quantum yield was determined by comparison with isomerization of *cis*-cyclooctene.

Light intensity dependence of the formation of 3

Perfluorohexane solutions of (*E*)-**1** were irradiated with a low pressure mercury lamp equipped with ND filters (60, 49, 30 and 17%) for 20 min.

Preparation of (*Z*)-rich 1

A hexane solution of (*E*)-**1** (1.01×10^{-2} mol l^{-1}, 30 ml) was irradiated at 370 nm light with a 500 W Xe lamp for 2 h. The reaction mixture was dried *in vacuo* to remove solvent. The ratio of *trans*- and *cis*-isomer was determined by ^{19}F NMR measurement (*trans*:*cis* = 1.00:1.46) in $CDCl_3$ (internal standard: $CFCl_3$). The (*Z*)-rich **1** prepared was used for photoreaction without purification.

References

1 R. Filler and Y. Kobayashi, *Biological Aspects of Fluorine Chemistry*, Elsevier Biomedical Press and Kodansha Ltd., 1982; R. E. Banks, *Organofluorine Chemicals and their Industrial Applications*, Ellis Horwood, London, 1979.

2 M. Yoshida and N. Kamigata, *J. Fluorine Chem.*, 1990, **49**, 1; W. R. Dolbier, Jr., *Chem. Rev.*, 1996, **96**, 1557; H. Sawada, *Chem. Rev.*, 1996, **96**, 1779; T. Umemoto, *Chem. Rev.*, 1996, **96**, 1757 and references therein.

3 J. G. Calvert and J. N. Pitts, *Photochemistry*, Wiley, New York, 1996; P. S. Engel and C. Steel, *Acc. Chem. Res.*, 1973, **6**, 275; P. S. Engel, *Chem. Rev.*, 1980, **80**, 99.

4 W. Adam and O. De Lucchi, *Angew. Chem.*, *Int. Ed. Engl.*, 1980, **19**, 762 and references therein.

5 I. M. Whittemore, A. P. Stefani and M. Szwarc, *J. Am. Chem. Soc.*, 1962, **84**, 3799.

6 W. J. Chambers, C. W. Tullock and D. D. Coffman, *J. Am. Chem. Soc.*, 1962, **84**, 2337.

7 W. Adam, F. Mazenod, Y. Nishizawa, P. S. Engel, S. A. Baughman, W.-K. Chae, D. W. Horsey, H. Quast and B. Seiferling, *J. Am. Chem. Soc.*, 1983, **105**, 6141.

8 T. Nakamura and A. Yabe, *Chem. Lett.*, 1994, 1573.

9 W. Adam and T. Openländer, *Angew. Chem.*, *Int. Ed. Engl.*, 1986, **25**, 661.

10 K. J. L. Paciorek, R. H. Kratzer, J. H. Nakahara and H. M. Atkins, *J. Fluorine Chem.*, 1991, **53**, 355.

11 It has been reported that tetrakis(perfluoroethyl)hydrazine was formed during photolysis of perfluoroazoethane which acts as a good radical scavenger. G. Kaupp and O. Sauerland, *J. Photochem. Photobiol. A: Chem.*, 1991, **56**, 375.

12 S. M. Pereira, G. P. Savage and G. W. Simpson, *Synth. Commun.*, 1995, **25**, 1023.

13 M. B. Robin, in *Higher Excited States of Polyatomic Molecules*, Academic Press, New York, 1974, vol. 1, p. 178–191; A. Maciejewski, *J. Photochem. Photobiol. A: Chem.*, 1990, **51**, 87.

14 W. A. Herrmann and C. W. Kohlpainter, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 1524; I. T. Horvath and J. Rabai, *Science*, 1994, **266**, 72.

15 H. Walter, D. E. Brooks and D. Fisher, *Partitioning in Aqueous Two-Phase Systems*, Academic Press, 1985; P. Racay, R. Kubinec and R. Cech, *J. Radioanal. Nucl. Chem. Letters*, 1996, **212**, 241.

16 This quantum yield was measured upon 185 nm irradiation of 11.27 mW cm^{-2}.

17 Ichinose *et al.* reported decomposition of adamantan-2-one by two-photonic excitation. N. Ichinose and S. Kawanishi, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2017.

18 T. Fuchikami and I. Ojima, *J. Fluorine Chem.*, 1983, **22**, 541; T. Umemoto, Y. Kuriu and H. Shuyama, *Chem. Lett.*, 1981, 1663; G. J. Chen and C. Tamborski, *J. Fluorine Chem.*, 1989, **43**, 207; T. Umemoto and Y. Gotoh, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 439.

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