CHEMISTRY LETTERS, pp. 1573-1576, 1994.

Perfluoroalkylation of Benzene by 185 nm Photolysis of Perfluoroazooctane

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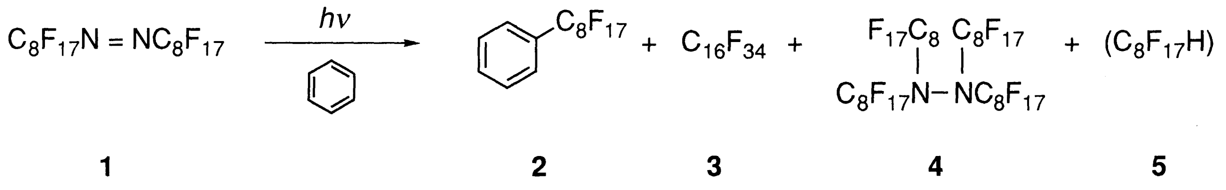
Perfluoroazooctane was photolyzed in benzene upon low pressure Hg lamp irradiation to generate perfluorooctyl radicals, which reacted with an excess of benzene to afford perfluorooctylbenzene. The investigation on the wavelength and light intensity dependence revealed that this photolysis proceeded effectively upon 185 nm irradiation by two photon absorption.

Much attention has been focused on perfluoroalkyl-containing organic compounds because of their unique properties, particularly in the field of medicinal chemistry and material science.[1] The introduction of perfluoroalkyl groups into organic compounds by thermal- and photo-induced radical species is the subject of many researches in organofluorine chemistry.[2] The photochemical generation of perfluoroalkyl radicals from perfluoroalkylhalides, perfluoroalkanesulfonyl chlorides, and perfluoroalkylmetallic reagents have been reported by many workers to date.[2]

Azo compounds are widely used in the synthesis of unusual organic molecules as precursors of carbon-centered radicals which are generated effectively upon UV irradiation.[3] However, there are few reports on perfluoroalkylation of organic compounds by the photolysis of perfluoro azo compounds.[4] Whittemore et al. investigated the relative rate constants of addition of CF_3 radicals to a variety of substituted benzenes by the photolysis of hexafluoroazomethane, but did not report the reaction mechanism of the photolysis of perfluoroazoalkanes in detail.[4a] We would like to report here the introduction of perfluorooctyl radicals into benzene by the photolysis of perfluoroazooctane (**1**) in benzene upon UV irradiation, and the dependence of product yields upon irradiation wavelength and intensity in this reaction system.

Perfluoroazooctane (**1**) was prepared according to the literature procedures.[5] UV-vis spectrum of **1** in hexane is shown in Fig. 1, indicating that azo group of **1** absorbs light at λ_{max} 188 nm (π-π^*) and λ_{max} 380 nm (n-π^*). As the π-π^* absorption of **1** has a much intense molar extinction coefficient (ε 23100) than n-π^* one (ε 30), it was expected that vacuum ultraviolet irradiation would lead to effective denitrogenation of **1**.[6]

Benzene solutions of **1** (1×10^{-3} mol dm^{-3}) in a suprasil cell (optical path : 1 cm) were irradiated with a 60 W low pressure Hg lamp (Eikohsha EL-S-SQ-60) without any filters under a nitrogen atmosphere. This



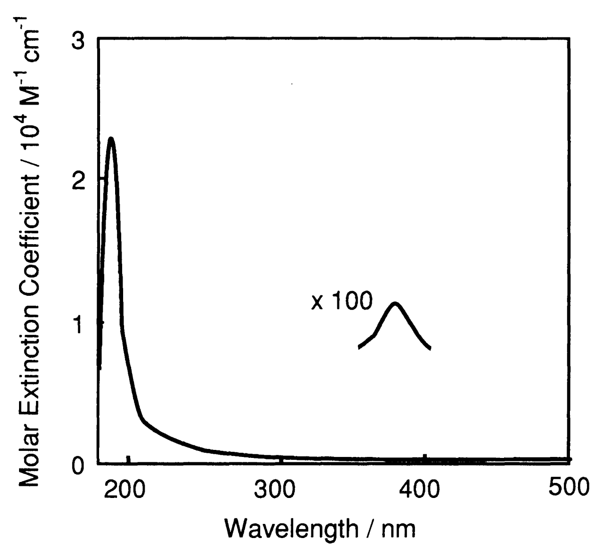


Fig. 1. UV-vis spectrum of **1** in hexane.

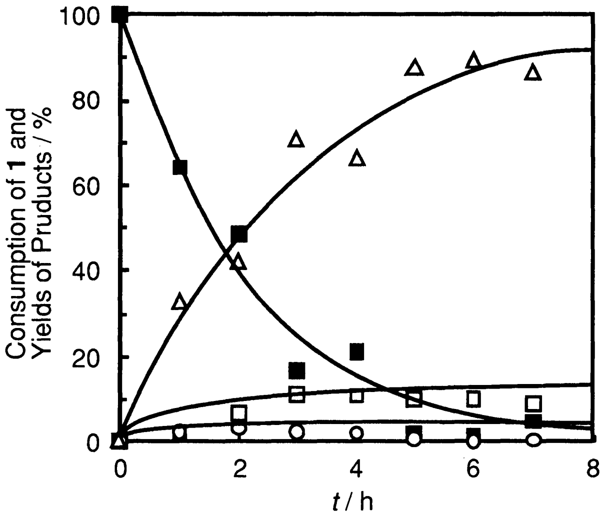
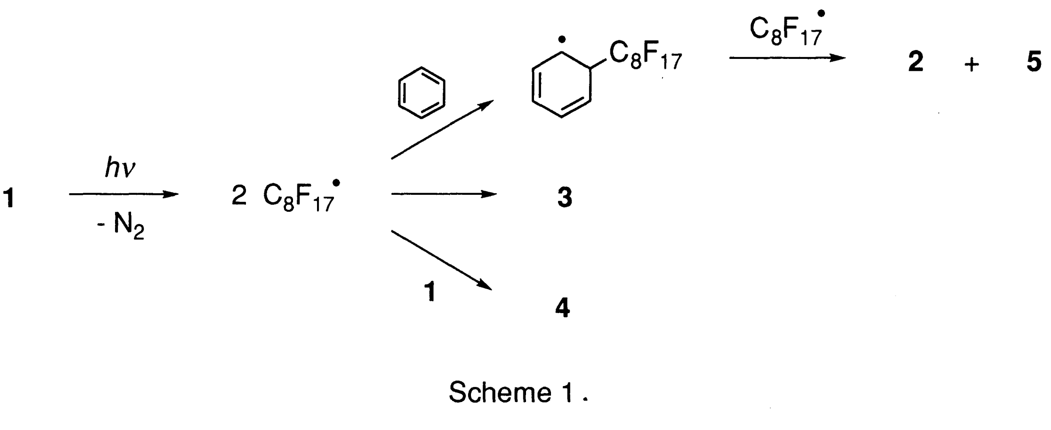


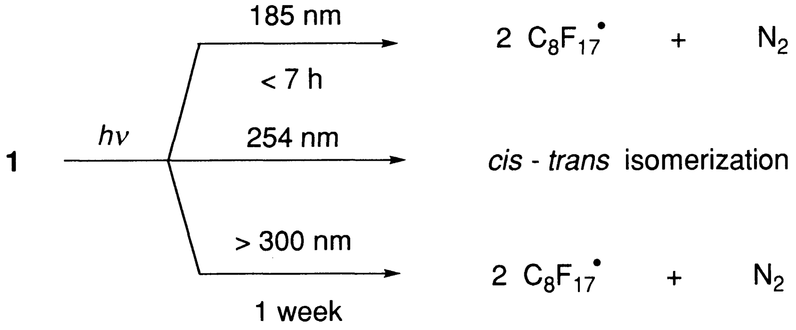
Fig. 2. Photolysis of **1** in benzene with a low pressure Hg lamp. ■, **1**; □, **2**; ○, **3**; △, **4**.

photoreaction was carried out at 50 °C because of the low solubility of **1** in benzene. Since **1** is stable on heating at 50 °C, thermolysis of **1** did not occur in the dark.7) The reaction was monitored by GC-MS with nonane and undecane as internal standards of **1** and perfluorooctylbenzene (**2**), respectively. The consumption of **1** and the formation of products are shown in Fig. 2. The desired perfluorooctylbenzene8) (**2**) which was formed from the reaction of perfluorooctyl radicals with an excess amount of benzene, and tetrakis(perfluorooctyl)hydrazine9) (**4**) were obtained, together with a small amount of perfluorohexadecane (**3**) which was formed by dimerization of perfluorooctyl radicals. The hydrazine **4** was obtained by the reaction of remaining substrate **1** with perfluorooctyl radicals. The high yields of **4** would be explained by the low concentration of the resulting perfluorooctyl radicals9) because most of photons were absorbed by benzene, and also by a localized high concentration of **1** because perfluoroalkyl-containing compound **1** was not entirely homogeneous in benzene. An equimolar amount of 1H-perfluorooctane (**5**) with **2** would be also formed by hydrogen abstraction of perfluorooctyl radicals, but unfortunately could not be detected by GC-MS because of its low boiling point.



Scheme 1.

The wavelength dependence of the photolysis of **1** was examined in this reaction, as shown in Scheme 2. In the case of >300 nm irradiation with a 500 W high pressure Hg lamp (USH-500D) through a filter (Toshiba UV-31), the photolysis of **1** occurred very slowly in spite of the focused irradiation with a lens for a week. Kaupp and Sauserland also reported the photolysis of perfluoroazoethane upon a very intense irradiation with XeCl excimer laser (308 nm).[9] Irradiation of 254 nm wavelength with the low pressure Hg lamp using an filter (Toshiba UV-21) for 7 h resulted in not the photolysis of **1** to perfluorooctyl radicals, but predominantly cis-trans isomerization of **1**. These results show that 185 nm irradiation is much more effective for the photolysis of **1**, compared with 254 or >300 nm light.[6] It is well-known that cyclic azoalkanes are smoothly denitrogenated on irradiation at 185 nm (π-π^* excitation), while they are reluctant to denitrogenate at 350 nm (n-π^* excitation).[10] It is interesting that perfluoroazoalkanes were also found to be reluctant to lose nitrogen similarly to cyclic azoalkanes.



Scheme 2.

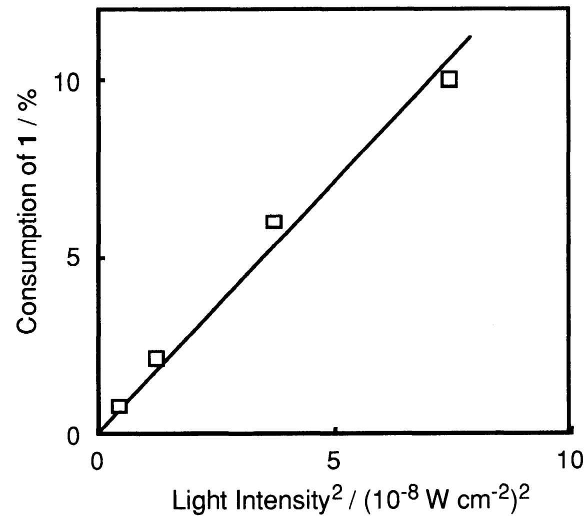


Fig. 3. The light intensity dependence of the photolysis of **1** upon 185 nm irradiation.

The light intensity dependence of the photolysis of **1** was also investigated. Benzene solutions of **1** were irradiated with the low pressure Hg lamp through ND filters for 1 h at 50 °C. As shown in Fig. 3, the photolysis of **1** changed in proportion to the square of the light intensity. These results indicate that two photons are required for the photolysis of **1** upon 185 nm irradiation. This consideration is consistent with Kaupp and Sauerland's report that high intensity irradiations with an excimer laser (XeCl 308 nm) gave the high concentration of pentafluoroethyl radicals by two photon absorption of perfluoroazoethane during the pulse.[9]

Since benzene exhibits its absorption maxima at 180 nm (ε 60000), most of photons are absorbed by an excess amount of benzene upon 185 nm irradiation in this reaction system. The important problems of the photoisomerization of benzene[11)] and of the energy transfer process from the excited benzene[12)] to **1** must be considered. In the former problem although isomer products of benzene such as fulvene were formed upon low pressure Hg lamp irradiation of the benzene solution of **1**, the reaction of these isomers with perfluorooctyl radicals was not observed. In the latter problem, the concentration dependence of the photolysis of **1** in benzene (from 1×10^{-5} to 1×10^{-2} mol dm^{-3}) was examined upon the low pressure Hg lamp irradiation for 1 h. The variation in the concentration of **1** did not affect the generation of perfluorooctyl radicals in the photolysis of **1**. Moreover, the wavelength dependence in this reaction system was not only observed in benzene of **1** upon irradiation, but also in hexane (1×10^{-3} mol dm^{-3}). Therefore, these results suggest that **1** was directly excited upon 185 nm irradiation into higher singlet excited states to generate perfluorooctyl radicals.

Further investigations on the reaction of perfluoroazooctane with alkanes upon low pressure Hg lamp or ArF excimer laser (193 nm) irradiation, and on the application to the field of material science are now in progress.

We would like to thank Professor Y. Inoue (Himeji Institute of Technology) for helpful suggestions and Perkin-Elmer Japan Co., Ltd. for measurements of UV-vis spectra.

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.*, **49**, 1 (1990).

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

4) I. M. Whittemore, A. P. Stefani, and M. Szwarc, *J. Am. Chem. Soc.*, **84**, 3799 (1962); P. Gölitz and A. de Meijere, *Angew. Chem., Int. Ed. Engl.*, **16**, 854 (1977).

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

6) 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.*, **105**, 6141 (1983).

7) T. H. McGee and C. E. Waring, *J. Phys. Chem.*, **73**, 2838 (1969); M. Rossi and D. M. Golden, *Int. J. Chem. Kine.*, **11**, 775 (1979).

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

9) G. Kaupp and O. Sauerland, *J. Photochem. Photobiol. A: Chem.*, **56**, 375 (1991).

10) W. Adam and T. Oppenländer, *Angew. Chem., Int. Ed. Engl.*, **25**, 661 (1986) and references therein.

11) H. R. Ward and J. S. Wishnok, *J. Am. Chem. Soc.*, **90**, 5353 (1968); N. Nakashima and K. Yoshihara, *J. Chem. Phys.*, **79**, 2727 (1983); I. J. Palmer, I. N. Ragazos, F. Bernardi, M. Olivucci, and M. A. Robb, *J. Am Chem. Soc.*, **115**, 673 (1993).

12) U. T. Bhalerao and M. Sridhar, *J. Chem. Soc., Chem. Commun.*, **1993**, 115.

(Received April 25, 1994)