A Direct Introduction of Perfluorooctyl Group into Cycloalkanes using the Photolysis of Perfluoroazooctane upon 185 nm Irradiation

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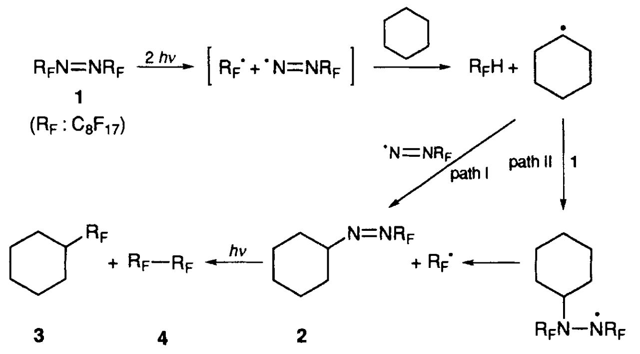
Perfluorooctyl-substituted cycloalkanes are prepared directly by photolysis of perfluoroazooctane in cycloalkanes upon 185 nm irradiation; a plausible mechanism is discussed on the basis of the time-course, quantum yield, and light intensity dependence during this photoreaction.

Perfluoroalkyl-substituted organic compounds exhibit pharmacological activity and water/oil repellent properties due to the presence of fluorine atoms, and are utilized as medicines and functional materials.[1] The methods for the preparation of perfluoroalkylated aromatic compounds have been developed using corresponding radicals by many groups.[2,3] However, few reports on the introduction of perfluoroalkyl group into alkanes have been published to date because of the following difficulties, namely the necessity of cooling down the reaction system and low yields of desired products.[4,5] In recent years, it has been found that perfluoroazoalkanes give rise to perfluoroalkyl radicals upon UV irradiation.[3,6] We would like to describe here a simple and direct preparation of perfluorooctyl-substituted cycloalkanes by means of the photolysis of perfluoroazooctane **1** in cycloalkanes upon 185 nm irradiation.

A typical experiment is described as follows. A cyclohexane solution of **1** (1 x 10^{-3} mol dm^{-1}) was irradiated with a 60 W low-pressure Hg lamp (Eikosha EL-S-SQ-60) at room temperature under a nitrogen atmosphere.† After irradiation for 1 h, the substitution of a hydrogen atom on cyclohexane for perfluorooctyl group took place efficiently to give perfluorooctylcyclohexane **3** in 76% yield, together with perfluorooctylazocyclohexane **2** as an intermediate to **3** (see below) and a small amount of perfluorohexadecane **4** from the recombination of perfluorooctyl radicals (Scheme 1).‡ Additionally, this photoreaction of **1** was carried out in cyclopentane and cycloheptane to give corresponding perfluorooctylcycloalkanes **5** and **6** in 78 and 70%, respectively (Table 1).

Since it was found that this method provided a general and simple perfluoroalkylation of cycloalkanes in good yields, it would be of interest to investigate this reaction mechanism by means of time-course, quantum yield, and light intensity dependence during this photoreaction in cyclohexane. First, the time-course of the consumption of **1** and of the formation of **3** and **4** during this photoreaction is shown in Fig. 1. From mass balance of **1**, **3** and **4** the existence of other products was indicated, namely an intermediate to give **3** and/or unknown byproducts. An experiment of this photoreaction of **1** upon the shorter irradiation (30 min) and separation of the reaction mixture with silica gel column chromatography gave only **2** besides **3** and **4**.§ The time-course results of the formation of **2** is also represented in Fig. 1. As a control experiment, isolated **2** was irradiated under the same condition as described above to give **3** in a quantitative yield.[5] Furthermore, a prolonged irradiation of this photoreaction (over 1 h) increased the formation of **3**. These results point out that **3** was formed *via* intermediate **2** obtained from the reaction of **1** with cyclohexane.



Scheme 1

Table 1 Preparation of perfluorooctylcycloalkanes using the photolysis of 1 in cycloalkanes[a]

Cycloalkanes	Yield (%)[b] Perfluoroalkylcycloalkanes	4
n = 0	**5**:78	2
n = 1	**3**:76	1
n = 2	**6**:70	1

[a] This photoreaction was carried out using 185 nm irradiation of 1 in cycloalkanes (1 × 10^{-3} mol dm^{-1}) for 1 h. [b] Yields of this photoreaction are not optimized.

Secondary, the light intensity dependence of this photoreaction indicated that the formation of intermediate **2** was proportional to the square of 185 nm light intensity ($\Phi = 0.11$) as shown in Fig. 2.[7] A plausible mechanism for the formation of **3** is represented in Scheme 1. The photolysis of **1** *via* two-photonic process resulted in cleavage of one C–N bond, followed by formation of a perfluorooctyldiazenyl radical and a perfluorooctyl radical,[8,9] which abstracted a hydrogen atom from cyclohexane to give a cyclohexyl radical.¶ Two pathways to achieve **2** are possible. One of them is the recombination of perfluorodiazenyl and cyclohexyl radicals (path I). However, path I is unlikely in this reaction system, as diazenyl radicals are generally so unstable at room temperature that they extrude nitrogen immediately to form perfluorooctyl radicals.[11] The other is as follows (path II): a cyclohexyl radical reacted with remaining **1**, and then elimination of a perfluorooctyl radical

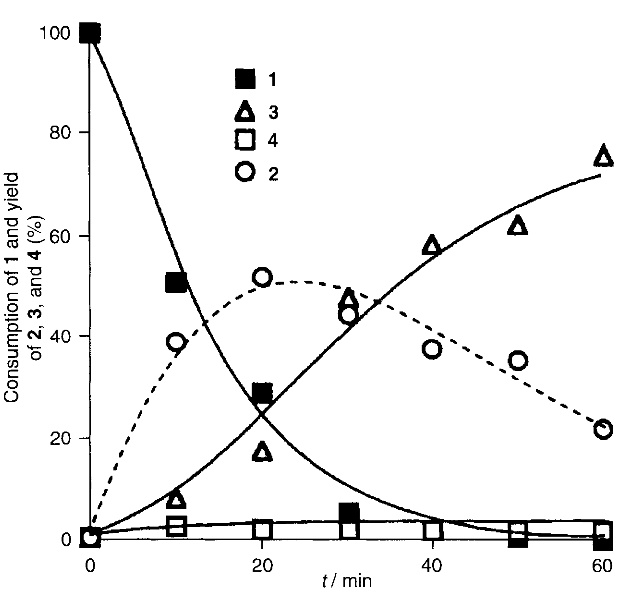


Fig. 1 The time-course of the photolysis of 1 in cyclohexane upon 185 nm irradiation

from formed hydrazyl radical afforded **2**. Path II seems to be likely since Batt *et al.* reported that the reaction of methyl radicals and hexafluoroazomethane took place by the mechanism similar to that described above.[12] Moreover, this mechanism is supported by the results that perfluoroazoalkanes are efficient radical scavengers.[3,6] Ultimately, the extrusion of nitrogen from **2** took place to give **3** upon the irradiation.

In conclusion, a feasible method for the preparation of perfluoroalkyl-substituted cycloalkanes was developed by means of the two-photonic photolysis of **1** upon 185 nm irradiation. Further investigations on the present reaction using an ArF excimer laser (193 nm) which is more favourable for multi-photonic processes are in progress.

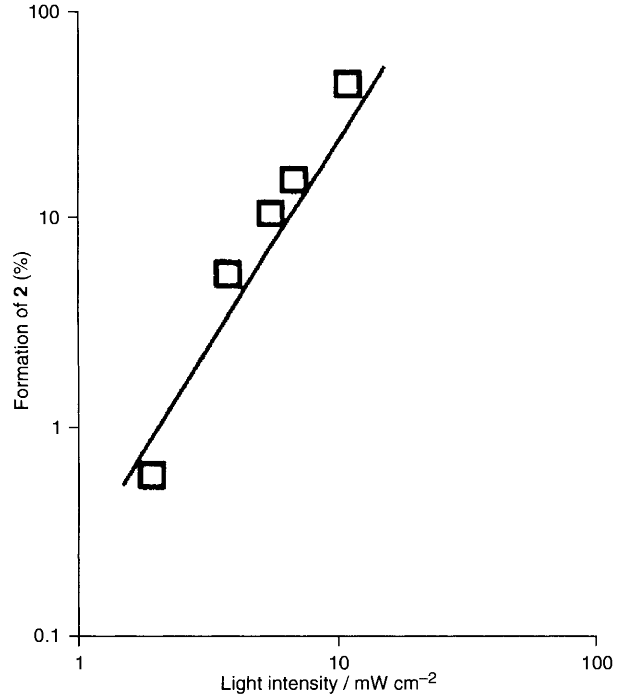


Fig. 2 The light intensity dependence of the formation of **2** upon 185 nm irradiation

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Footnotes

† Recently we reported that 185 nm irradiation was effective for the photolysis of **1**, compared with 254 nm irradiation.[3]

‡ Unfortunately 1H-perfluorooctane (R_FH) could not be detected by GC-MS because of its low boiling point.

§ Product **2** was assigned by measurements of ^{1}H NMR, IR, and MS: ^{1}H NMR ($CDCl_3$) δ 0.85–0.91 (m, 2 H), 1.10–1.43 (m, 4 H), 1.57–1.88 (m, 5 H); IR (neat) 2943, 2864, 1458, 1240, 1209, 1150 cm^{-1}; MS 511 ($M^+ - 19$).

¶ It is known that perfluoroalkyl radicals abstract hydrogen atom much faster than corresponding alkyl radicals (*ca.* 100 times).[10]

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