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Photosensitized Defluorination of Saturated Perfluorocarbons

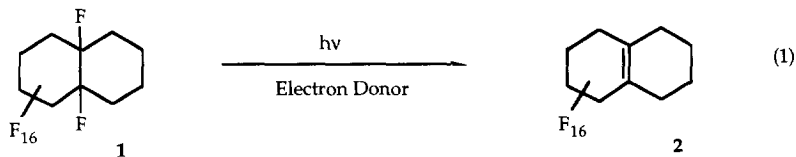
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Abstract: UV irradiation of perfluorodecalin **1** in the presence of an electron donor results in the facile formation of perfluoroolefin **2** from the selective elimination of the vicinal tertiary fluorines. Copyright © 1996 Elsevier Science Ltd

Introduction

Saturated perfluorocarbons (PFC's) are extremely inert materials with a wide variety of industrial and biomedical applications.^{1a, b} Thus, the discovery of new controlled reactions utilizing PFC's is challenging from both mechanistic and application points of view.^{1c} Mechanistically, photoinduced electron transfer to the electrophilic PFC is a potential process to initiate chemical modification.² A new method for partial reduction of PFC's by using mercury photosensitization and ammonia has recently been reported.³ A perfluoroolefin was proposed as the reactive intermediate resulting from the elimination of two fluorines. The intermediate, expected to be more reactive than the starting material, was not isolated. Herein, we report a photochemically induced reaction of perfluorodecalin **1**, which leads to the formation of perfluoroolefin **2** *via* selective defluorination (eq.1) and probably proceeds through an electron transfer mechanism. The product **2**, has been implicated in the *complete defluorination* of **1** by sodium arenethiolate.^{2e} The scope, mechanism, and limitations of reaction in eq. 1 and its relationship with the reaction of **1** with sodium arenethiolate are discussed.



Results and Discussion

Perfluorodecalin⁴ (**1**, 0.114 g, 2.5×10^{-4} mol) was irradiated in a Pyrex ($\lambda > 290$ nm) tube for *ca.* 4 h with a medium pressure Hg lamp (Hanovia, 450 W), in a biphasic solution (2ml) consisting of a 1:1 mixture of N, N-dimethylformamide (DMF) and hexanes. Reaction required the presence of various photosensitizing amines such as N, N, N', N'-tetramethyl-1, 4-phenylenediamine **3**, N, N, N', N'-tetramethylbenzidine **4**, 2, 3, 5, 6-tetramethyl-1, 4-phenylenediamine **5** and phenothiazine **6** (1.25×10^{-5} mol, *ca.* 1:20 ratio of amine to perfluorodecalin respectively). The reaction mixture was purged (10 min) with argon prior to and then stirred vigorously during irradiation. Upon completion of photolysis, the hexane phase was separated and analyzed by ¹⁹F NMR and GC-MS analysis.⁵ Hexadecafluoro-bicyclo[4.4.0]dec-1(6)-ene **2** was identified in the mixture as the only product from conversion of

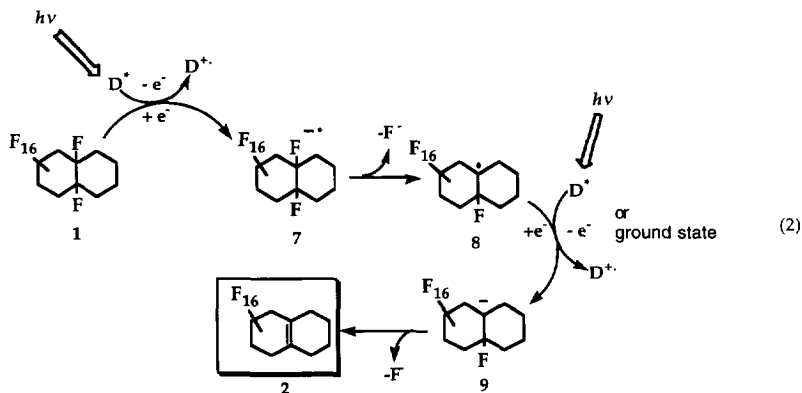
perfluorodecalin **1** by comparison with literature data.⁶ The highest conversion of starting material was obtained with amines **3** and **4**, which are known to be very good electron donors when photoexcited.^{7a,b} The yields for formation of **2** could be optimized (~60-70%) by increasing the concentration of the amine (ca. 1:8 molar ratio of amine to perfluorodecalin respectively) and extending the length of irradiation (>12 h). Representative yields are summarized in Table 1.

Table 1. Representative Yields of **2** from Irradiation of **1** with Various Donors.

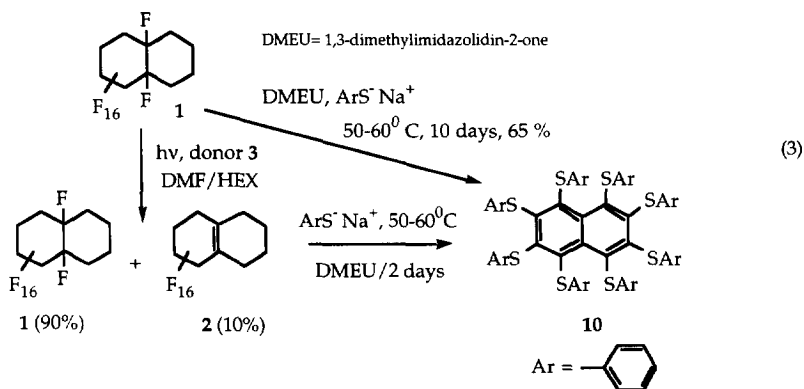
	Electron Donor (D)	$E^0(D^+/D)^a$	Yield of 2 (%) ^b
3		0.16	~35
4		0.32	~35
5		—	~22
6		0.76	~22

^a Redox potentials, V vs. SCE in acetonitrile. ^b The yields of **2** were not optimized and estimated from the ¹⁹F NMR of the hexane phase (see also ref 5). The ratio of amine: perfluorodecalin is ca. 1:20.

The defluorination is proposed to proceed *via* electron transfer ^{2, 8} (eq. 2) from the photoexcited amine (D^*) to **1** to form the radical anion **7** (possessing a σ^* antibonding electron).⁹ In the radical anion **7**, the inherently strong tertiary C-F bonds of **1** become labile toward dissociation to a carbon-centered radical **8** and fluoride ion. The requirement of the photosensitizer has been established by control experiments. Based on ¹⁹F NMR analysis, there was no formation of olefin **2** in the absence of amine. Also, upon irradiation of **1** in subsequent ESR experiments with N, N, N', N'-tetramethyl-1, 4-phenylenediamine and perfluorodecalin, signals which are attributable to the radical cation of the amine were observed.^{7a,b} Although we failed to observe any ESR signal from the carbon-centered radical **8**, it is a plausible intermediate resulting from loss of F⁻ from **7**.^{7c,d} A second electron, originating from either an excited or ground state amine is proposed to add to **8** to form carbanion **9**. Several radical anions of saturated perfluorocarbons have been observed as stable salts.¹⁰ The radical anion would plausibly generate **2** by eliminating a second F⁻. We are also concerned with the fate and stoichiometry of photosensitizer and evolution of fluoride as well, which are interesting mechanistic points.¹¹ Accordingly, we investigated the role of tertiary fluorines by reacting perfluoromethylcyclohexane and perfluoro-1,3-dimethylcyclohexane⁴ with amine **4**. Upon irradiation, neither perfluoromethylcyclohexane nor perfluoro-1,3-dimethylcyclohexane reacts to form perfluoroolefin (based on ¹⁹F NMR spectra). Hence we conclude that photosensitized elimination of two fluorines is most favorable for structures possessing two vicinal tertiary fluorines.



A striking reaction of sodium arenethiolate (albeit over several weeks) with perfluorodecalin leading to aromatization to **10** (eq. 3) *via* complete defluorination of **1** has been reported.^{2e} The authors suggested a sequential one-electron transfer mechanism and perfluoroolefin **2** as the critical intermediate. We were able to test this mechanistic proposal with the following experiments. Irradiation of perfluorodecalin with amine **3** in a molar ratio of 20:1, respectively, was carried up to 10% conversion. The hexane phase containing the mixture of **2** and **1** was then stirred with molecular excess of arenethiolate sodium salt (eq.3) following the published protocol.^{2e} The reaction mixture was analyzed after two days. However, the minimum time for completing the reaction has not yet been established. The isolated product was identified by comparison with literature data (¹H, ¹³C NMR and MS) to be **10**.¹² The ¹⁹F NMR of the crude reaction mixture after work-up did not show any traces of perfluorodecalin or any other fluorinated compound, implying that all starting material has been defluorinated to **10**. These results support the suggestion that perfluoroolefin **2** is indeed the critical intermediate that triggers the conversion of perfluorodecalin to **10**.



Conclusions

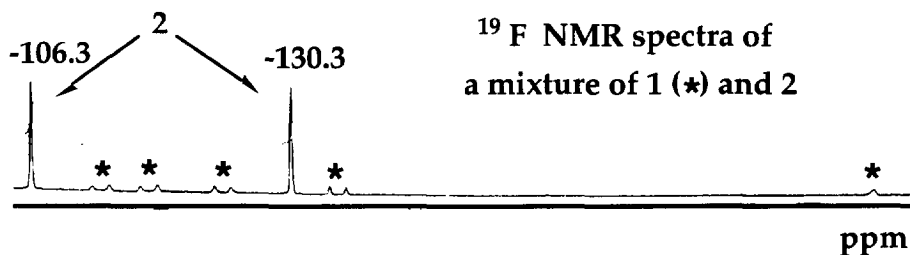
In summary, photoinduced electron transfer provides a potentially efficient method for elimination of a pair of fluorines from saturated perfluorocarbons possessing vicinal tertiary fluorines under mild conditions to form perfluoroolefins such as **2**. Perfluoroolefin **2** has been shown to be a plausible product and limiting intermediate in the

conversion of 1 to 10. Electron transfer induced reactions of PFCs could be relevant to their use as artificial blood substitutes, where they have been found to be generally non-toxic.^{13, 1b} The above findings provide further evidence in addition to those initially presented in reference 2e that perfluorochemicals should not be considered completely inert under all mild conditions, in particular for biological systems where electron donors are active.

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- Perfluorodecalin (mixture of *cis*- and *trans*-isomers), perfluoromethylcyclohexane and perfluoro-1,3-dimethylcyclohexane (mixture of *cis*- and *trans*-isomers) were purified by distillation before use. The UV spectra of all starting materials showed the absence of unsaturated impurities.
- The ¹⁹F NMR of the hexane phase showed two sharp singlets resonating at -106.3 and -130.1 ppm attributable to 2 along with the diminished resonances of 1 (see below). Shifts are given in reference to CFC13. GC-MS showed a peak at *m/e* = 424 which indicated the loss of two fluorines from 1.



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- (a) ¹H NMR and GC-MS analysis of the DMF phase in two cases (3, 4) suggested destruction of the donor amine. (b) The evolution of fluoride was detected by selective ion electrode in a similar case.^{2e} Presently we did not attempt to detect fluoride, and its evolution was assumed.
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