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PHOTOSUBSTITUTION REACTIONS ON AROMATIC AND HETEROAROMATIC RINGS EVIDENCE FOR ADDITION AND SUBSTITUTION MECHANISM

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Abstract

Irradiation of a cyclohexane solution of hexafluorobenzene in the presence of benzophenone resulted in both, substitution and addition products. Similar photoreaction has been observed by irradiation of hexafluorobenzene in some alcohols in the presence of benzophenone. The reaction of pentafluorobenzene with methanol or cyclohexane resulted in the substitution of a 2- or 4-fluoro atom, while the reaction of pentafluoroanisole resulted in the formation of o-, m- and p-isomers. Irradiation of a cyclohexane solution or of an alcohol solution of octafluoronaphthalene yielded 1- and 2-substituted products. On the other hand, the photosubstitution of fluorine atom in pentafluoropyridine took place exclusively at the position four, thus forming 4-cyclohexyl or 4-(1-hydroxyalkyl) substituted products.

Introduction

The classification of photochemical aromatic substitution reactions is based on the reaction type, the character of the excited state, or kinetics. Photochemical reactions in which the unsubstituted benzene molecule undergoes a substitution reaction are known, but in many of these cases the reactive species is not a benzene molecule in an excited state.[1] Bryce-Smith et al[2,3,4] found that benzene reacted with amines and pyrrole to yield the substituted benzenes. The reactive species appeared to be benzene in its excited state, but the primary products were mainly addition adducts rather than substitution products. Photochemical reactions of halogen-substituted benzenes involve the photochemical interchange of halogen atoms. Irradiation of bromobenzene[5] in benzene solution with the low-pressure mercury lamp led to biphenyl in a 40% yield, while some para-substituted bromobenzene derivatives afforded the corresponding 4-substituted biphenyls.[5] A similar reaction has been observed with substituted chlorobenzene.[6]

Photoreactions of fluorobenzene with a range of nucleophiles were also studied.[7] Irradiation of fluorobenzene in piperidine afforded N-phenyl piperidine in a 10% yield. In the photochemical reaction of fluorobenzene with methoxide ion in methanol solution, anisole was obtained in low yield. m-Fluoronitrobenzene undergoes photosubstitution in aqueous alkaline solution, yielding m-nitrophenolate.[8] Similar reactions took place when o- or p-fluoronitrobenzene[8] was used as a substrate. Brasem et al[8] have found that 2-fluoro-4-nitroanisole undergoes efficient photolysis in alkaline medium, in neutral, or even in weakly acidic solution, and the sole product formed was 2-methoxy-5-nitrophenol. The fluorine atom in 2-fluoro-4-nitroanisole was substituted under photochemical conditions with methoxide ion, ethoxide ion, propoxide ion, and isopropoxide ion.[8]

Heaney and coworkers[9] have shown that photolysis of 1,2-diiodotetrafluorobenzene in the presence of benzene or benzene-hexane mixture resulted in the formation of products which arose from 2-iodotetrafluorophenyl radical and from tetrafluorobenzyne.

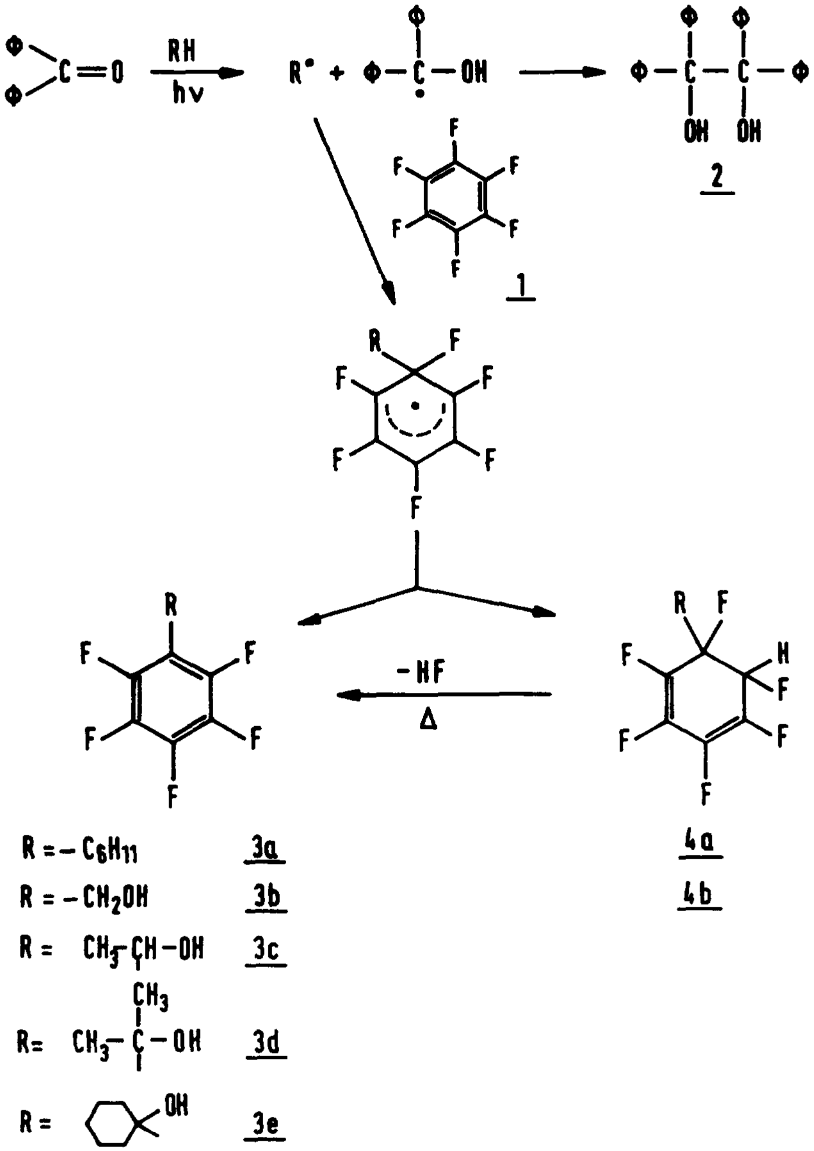
Irradiation of hexafluorobenzene[10] in cyclohexane or cyclooctane solution yielded hydrogen fluoride and a complex reaction mixture containing cyclohexyl or cyclooctylpentafluorobenzene and other radical coupling products.

Results and Discussion

We have previously reported that 24-h irradiation of a solution of hexafluorobenzene in cyclohexane in the presence of benzophenone at λ= 300-350 nm led to the formation of three products:[11] 1,1,2,2-tetraphenyl-1,2-dihydroxyethane (2), cyclohexylpentafluorobenzene (3a), and 1-cyclohexyl-1,2,3,4,5,6-hexafluoro-3,5-cyclohexadiene (4a). The mechanism suggested the initial formation of a cyclohexyl radical, which reacted with hexafluorobenzene, thus forming a radical species, which transformed further, by two different paths, to substitution and addition products (Scheme 1).

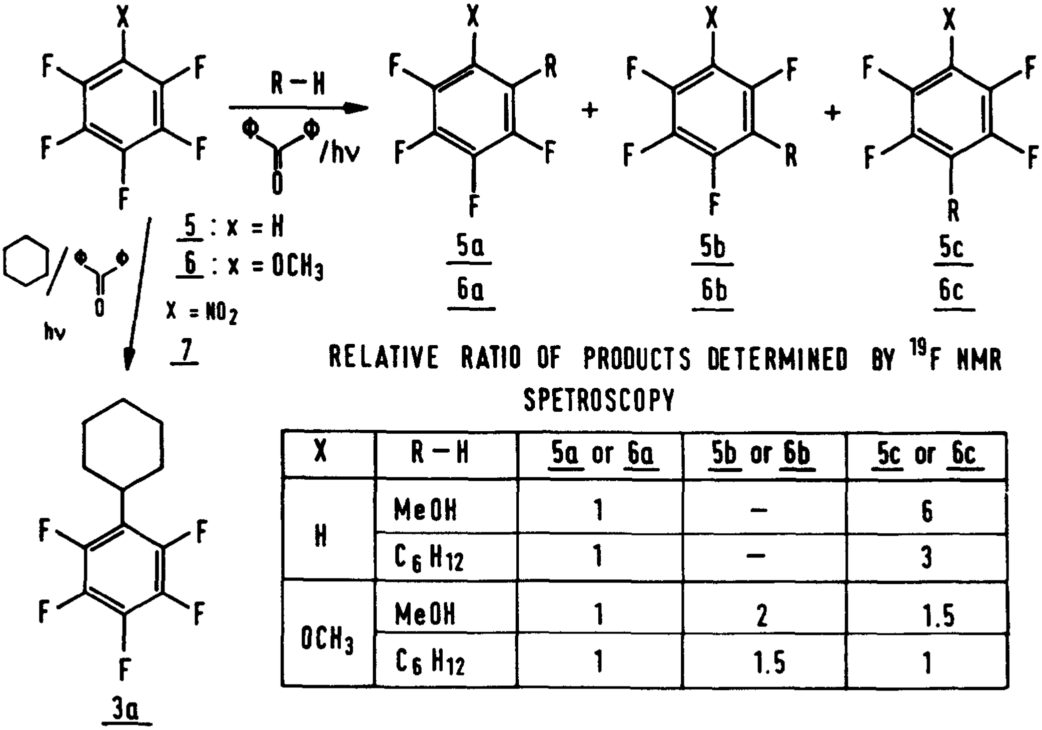
The reaction with cyclopentane in the presence of benzophenone resulted in the formation of 1-cyclopentyl-pentafluorobenzene, while the reaction with cycloheptane, under the above mentioned conditions, failed.

SCHEME 1



To determine the influence of the substituent in substituted pentafluorobenzene on the reaction pathway, we studied the reactions with pentafluorobenzene (5), pentafluoroanisole (6), and pentafluoronitrobenzene (7). The cyclohexane solution of pentafluorobenzene was irradiated in the presence of benzophenone at λ= 300-350 nm and the mixture of two products in the relative ratio of 1:3 was formed (Scheme 2). On the basis of their spectroscopic data (experimental section), we determined that substitution of fluorine atom ortho and para to the hydrogen atom took place with (2,3,4,5-tetrafluorophenyl) cyclohexane (5a) and (2,3,5,6-tetrafluorophenyl) cyclohexane (5c) formation. No meta-substituted product or product with substitution of hydrogen atom was observed.

SCHEME 2



RELATIVE RATIO OF PRODUCTS DETERMINED BY ^{19}F NMR SPETROSCOPY

X	R − H	5a or 6a	5b or 6b	5c or 6c
H	MeOH	1	–	6
	C_6H_{12}	1	–	3
OCH_3	MeOH	1	2	1.5
	C_6H_{12}	1	1.5	1

Irradiation of 0.028 M cyclohexane solution of pentafluoroanisole (6) resulted in the formation of three isomers with the ratio of o- : m- : p- being 1:1.5:1 (Scheme 2). The structures of the products were determined on the basis of their spectroscopic data. We also studied the reaction of pentafluoronitrobenzene (7) with cyclohexane and the formation of cyclohexylpentafluorobenzene (3a) was observed as the sole product, indicating that only ipso substitution took place.

Photosubstitution reaction of hexafluorobenzene also took place in methanol solution[12] when irradiated in the presence of benzophenone at λ= 300-350 nm and the mixture of 1,1,2,2-tetraphenyl-1,2-dihydroxyethane (2), hydroxymethylpentafluorobenzene (3b), and 1-hydroxymetyl-1,2,3,4,5,6-hexafluoro-3,5-cyclohexadiene (4b) was obtained (Scheme 1). Reduction of irradiation time from 24 hours to 6 hours or prolongation to 60 hours affected only the combined yield of the products, but not the ratio of the substitution to addition products.

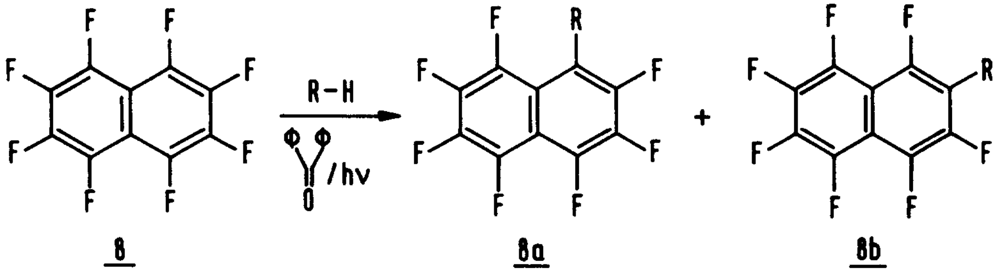
Since we were interested in the effect of the structure of the alcohol on the photoreaction, we studied the reactions in ethanol, isopropanol, and cyclohexanol and found that the coresponding hydroxyalkyl derivatives (3c, 3d, 3e) were formed in all cases (Scheme 1).

We also studied the effect of the substituent in benzene ring on the photoreaction pathway and pentafluorobenzene, and pentafluoroanisole were chosen as substrates. Irradiation of pentafluorobenzene in methanol under the same reaction conditions as in the case of hexafluorobenzene resulted in the substitution of fluorine atom at ortho or at para position to the hydrogen atom with hydroxymethyl group. No meta isomer was detected (Scheme 2). The reaction of pentafluoroanisole with methanol resulted in the formation of the o-, m-, and p-isomers of hydroxymethyl-tetrafluoroanisole in the ratio of 1:2:1.5 (Scheme 2).

We were also interested in the influence of the structure of the aromatic ring on the course of photosubstitution reaction and octafluoronaphthalene was chosen as substrate. A 24-hour irradiation of a cyclohexane solution in the presence of benzophenone resulted in low conversion of the starting compound, while prolongation of the reaction time increased the conversion. We tried to separate the products of the crude reaction mixture using several methods, but we were not successful. On the basis of mass spectrum and ^{19}F nmr and ^{1}H nmr spectra of the reaction mixture, we could determine that monosubstitution of fluorine atom at position 1- and 2- took place (Scheme 3). The same results were obtained when alcohol solutions (methanol, ethanol, 2-propanol) of octafluoronaphthalene were irradiated but in all cases we were unable to isolate pure 1- and 2-substituted products.

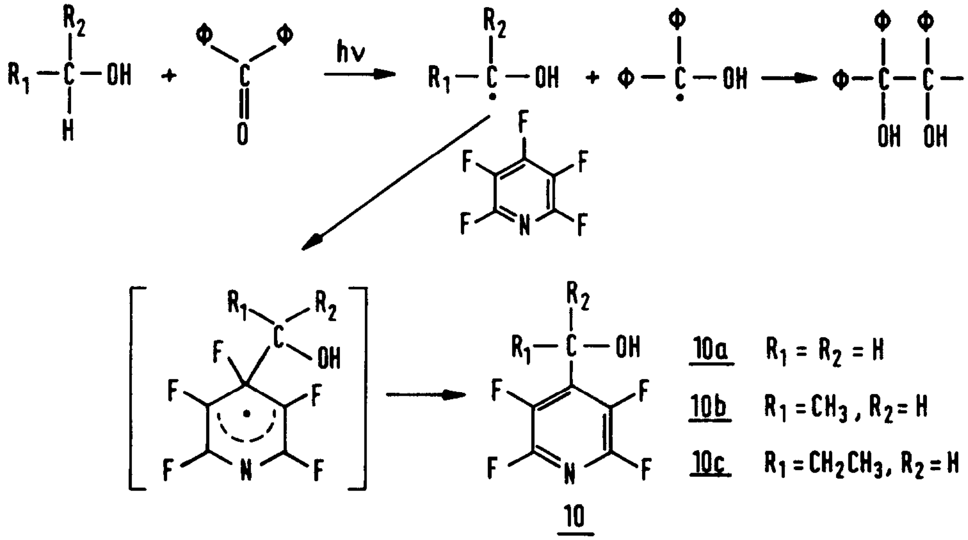
Bryce-Smith et al[13] have also investigated the reaction of 2-fluoropyridine with diethylamine which gave exclusively the N-substituted products while the product of cine-substitution was not detected. The photoreaction of 2-fluoropyridine and triethylamine yielded a 2:1 mixture of 2-diethylaminopyridine and N,N-diethyl-1-(2-pyridyl)ethylamine.

SCHEME 3



Since it was determined that UV irradiation of hexafluorobenzene or substituted pentafluorobenzenes in cycloalkane or several alcohol solutions in the presence of benzophenone resulted in the formation of addition and substitution products, we found it instructive to study reactions with pentafluoropyridine under the above mentioned conditions. Irradiation of a cyclohexane solution of pentafluoropyridine[14] in the presence of benzophenone resulted in the formation of 4-cyclohexyl-tetrafluoropyridine (9), while no addition product was observed. We also studied the reactions of pentafluoropyridine in alcohol solutions.[15] Irradiation in methanol or ethanol or n-propanol solution in the presence of benzophenone resulted in regiospecific substitution of the fluorine atom at position four, thus

SCHEME 4



forming the corresponding hydoxyalkyl derivatives (10a, 10b, 10c, Scheme 4). On the other hand, reaction in 2-propanol or in cyclohexanol resulted in 4-substituted products in very low yield, while no reaction was observed in t-butyl alcohol.

Based on the results obtained, we suggested the following mechanism: in the presence of benzophenone, the hydroxyalkyl radical is formed, which reacts with pentafluoropyridine, thus forming the radical species, which is further transformed into the 4-substituted products (Scheme 4).

Experimental

Irradiation was carried out in a Rayonet Photochemical Chamber, Reactor Model RPR-100, with RPR 300 nm and RPR 350 nm lamps. IR spectra were recorded by using a Perkin-Elmer 257 spectrometer, ^1H and ^{19}F NMR spectra were determined by a JEOL JNM-PS-100 spectrometer from CCl_4 or $CDCl_3$ solution with Me_4Si and CCl_3F as internal standards. Mass spectra were recorded on a CEC 21-110 spectrometer. Melting points were determined on a Kofler apparatus and are uncorrected. Gas liquid chromatography was carried out on a Varian Aerograph Model 1800 and preparative TLC on Merck PSC-Fertigplatten Kieselgel F254.

Materials

Hexafluorobenzene, pentafluorobenzene, pentafluoroanisole, pentafluoronitrobenzene, pentafluoropyridine, octafluoronaphthalene, and benzophenone were obtained from commercial sources. Solvents were purified by established methods and stored over molecular sieves.

General Procedure

1 Mmol of substrate and 2 mmols (364 mg) of benzophenone were dissolved in 18 ml of the appropriate solvent. The solution was irradiated at room temperature for 24 hours with 300-350 nm lamps. A white crystalline 1,1,2,2-tetraphenyl-1,2-dihydroxyethane (2), precipitating when the solution was evaporated in vacuo to one third of its volume, was filtered off. The filtrate was evaporated under reduced presure and the crude reaction mixture was analysed by ^{19}F nmr spectroscopy and separated by

preparative glc or tlc.

Irradiation of Hexafluorobenzene in Methanol

The crude reaction mixture was separated by preparative tlc (SiO_2, mobile phase: petroleum ether : $CHCl_3$ 95:5) and 95 mg (48%) of hydroxymethylpentafluorobenzene (3b) and 40 mg (20%) of 1-hydroxymethyl-1,2,3,4,5,6-hexafluoro-3,5-cyclohexadiene (4b) were isolateted as oily products.

Spectroscopic data of hydroxymethylpentafluorobenzene (3b):
^{19}F nmr spectrum: δ= -150.0 (2F, dd, J= 24; 9Hz, F-2, F-6), -159.75 (1F, t, J= 24Hz, F-4), -168.0 ppm (2F, td, J= 24; 9Hz, F-3, F-5); ^1H nmr (CCl_4): δ= 4.76 (2H, s, $-CH_2-$), 3.61 ppm (1H, broad singlet, -OH); mass spectrum calcd. for $C_7F_5H_3O$ m/z 198.0104, found m/z 198.0104, m/z 198 (M^+, 100%), 181(65), 179(19), 177(57), 150(36), 117(24), 99(22).

Spectroscopic data of 1-hydroxymethyl-1,2,3,4,5,6-hexafluoro-3,5-cyclohexadiene (4b):
^{19}F nmr spectrum: δ= -139.5 (2F, dm, J= 27Hz), -154.9 (2F, dm, J= 27Hz), -167.25 (1F, td, J=24; 24Hz, F-1), -169.9 ppm (1F, dd, J= 50; 24 Hz, F-2); ^1H nmr: δ= 4.5 (1H, dm, J= 50Hz), 4.2 ppm (2H, s, $-CH_2-$). We were unable to obtain the mass spectrum of the addition product because under the conditions used in mass spectrometry method, elimination of hydrogen fluoride took place and only the mass spectrum of hydroxymethylpentafluorobenzene was detected.

Irradiation of Hexafluorobenzene in Ethanol

The crude reaction mixture was separated by preparative glc (FFAP 30% on CHROM A/W at 200°C) and 60 mg (28%) of 1-pentafluorophenyl ethanol (3c) was obtained.

Spectroscopic data:
^{19}F nmr spectrum: δ= -147.0 (2F, dd, J= 24; 9Hz, F-2, F-6), -157.5 (1F, t, J=24Hz, F-4), -161.25 pm (2F, td, J= 24; 9Hz, F-3, F-5); ^1H nmr (CCl_4): δ= 1.58 (3H, d, J= 6Hz, $-CH_3$), 2.28 (1H, broad singlet, -OH), 5.05 ppm (1H, q, J= 6Hz, -CH); mass spectrum calcd. for $C_8F_5H_5O$ m/z 212.0261, found m/z 212.0260, m/z 212 (M^+, 42%), 198(17), 197(100), 196(14), 149(14) 99(13), 45(15).

Irradiation of Hexafluorobenzene in 2-Propanol

Separation of the crude reaction mixture by preparative glc (FFAP 30% on CHROM A/W at 190°C) yielded 60 mg (26%) of 1-methyl-1-(pentafluorophenyl) ethanol (3d).

Spectroscopic data:
^{19}F nmr spectrum: δ= -145.5 (2F, dd, J= 24; 9Hz, F-2, F-6), -162.75 (1F, t, J= 24 Hz, F-4), -168.0 ppm (2F, td, J= 24; 9Hz, F-3, F-5); ^1H nmr (CCl_4): δ= 1.78 (6H, s, $-CH_3$), 3.12 ppm (1H, broad singlet, -OH); mass spectrum calcd. for $C_9F_5H_7O$ m/z 226.0417, found m/z 226.0415, m/z 226 (M^+, 3%), 211(100%), 182(20), 167(12), 43(38).

Irradiation of Hexafluorobenzene in Cyclohexanol

The crude reaction mixture was separated by preparative glc (FFAP 30% on CHROM A/W at 210°C) and 80 mg (30%) of 1-(pentafluorophenyl) cyclohexanol (3e) was isolated.

Spectroscopic data:
^{19}F nmr spectrum: δ= -142.5 (2F, dd, J= 24; 9Hz, F-2, F-6), -159.0 (1F, t, J= 24Hz, F-4), -164.25 ppm (2F, td, J=24; 9Hz, F-3, F-5); ^1H nmr (CCl_4): δ= 1.47-2.17 (10H, m, $-CH_2-$), 2.37 ppm (1H, broad singlet, -OH); mass spectrum calcd. for $C_{12}F_5H_{11}O$ m/z 266.0730, found m/z 266.0738, m/z 266 (M^+, 18%), 224(38), 210(43), 182(100), 167(20), 86(51), 84(76), 51(41), 49(36).

Irradiation of Pentafluorobenzene in Cyclohexane

The crude reaction mixture was separated by preparative glc (FFAP 30% on CHROM A/W at 175°C) and 20 mg (9%) of (2,3,4,5-tetrafluorophenyl) cyclohexane (5a) and 68 mg (30%) of (2,3,5,6-tetrafluorophenyl) cyclohexane (5c) were obtained.

Spectroscopic data of (2,3,4,5-tetrafluorophenyl) cyclohexane (5a):
^{19}F nmr spectrum: δ= -120.8 (1F, m, F-5), -134.2 (1F, t, J= 24Hz, F-4), -139.5 (1F, dd, J= 24; 9Hz, F-2), -166.5 ppm (1F, td, J= 24; 6Hz, F-3), ^1H nmr (CCl_4): δ= 6.72 (1H, m, aromatic H), 2.75 (1H, m, cyclohexyl H), 1.02-1.98 ppm (10H, m, $-CH_2-$); mass spectrum calcd. for $C_{12}F_4H_{12}$ m/z 232.0875, found m/z 232.0876, m/z 232 (M^+, 24%), 84(93), 69(24), 56(100), 42(31).

Spectroscopic data of (2,3,5,6-tetrafluorophenyl) cyclohexane (5c):
^{19}F nmr spectrum: δ= -142.5 (2F, ddd, J= 24; 9; 9Hz, F-2, F-6), -146.5 ppm (2F, m, F-3, F-5); ^{1}H nmr (CCl$_4$): δ= 6.42 (1H, t, J= 9Hz, aromatic H), 2.8 (1H, m, cyclohexyl H), 1.04-1.92 ppm (10H, m, -CH$_2$-); mass spectrum calcd. for $C_{12}F_4H_{12}$ m/z 232.0875, found m/z 232.0876, m/z 232(M$^+$, 24%), 84(93), 69(24), 56(100), 42(31).

Irradiation of Pentafluorobenzene in Methanol
Separation by preparative glc (FFAP 30% on CHROM A/W at 190°C) gave 14 mg (8%) of (2,3,4,5-tetrafluorophenyl) methanol (5a) and 80 mg (44%) of (2,3,5,6-tetrafluorophenyl) methanol (5c).

Spectroscopic data of (2,3,4,5-tetrafluorophenyl) methanol (5a):
^{19}F nmr spectrum: δ= -122.3 (1F, m, F-5), -135.1 (1F,t, J= 24Hz, F-4), -140.3 (1F, dd, J=24; 9Hz, F-2), -168 ppm (1F, td, J= 24; 6Hz, F-3); ^{1}H nmr: δ= 7.2 (1H, m, aromatic H), 4.57 (2H, s, -CH$_2$-), 2.42 ppm (1H, broad singlet, -OH); mass spectrum calcd. for $C_7F_4H_4O$ m/z 180.0198, found m/z 180.0198, m/z 182(M$^+$+2, 59%), 180(M$^+$, 20), 167(31), 105(100), 77(79), 51(41).

Spectroscopic data of (2,3,5,6-tetrafluorophenyl) methanol (5c):
^{19}F nmr spectrum: δ= -141.0 (2F, dt, J= 24, 9Hz, F-3, F-5), -147 ppm (2F, dm, J= 24Hz, F-2, F-6); mass spectrum calcd. for $C_7F_4H_4O$ m/z 180.0198, found m/z 180.0198, m/z 182(M$^+$+2, 68%), 180(M$^+$, 88), 163(60), 159(64), 77(100), 51(60).

Irradiation of Pentafluoroanisole in Cyclohexane
After separation by preparative glc (FFAP 30% on CHROM A/W at 200°C) 22 mg (8%) of (2,3,4,5-tetrafluoro-6-methoxyphenyl) cyclohexane (6a), 26 mg (10%) of (2,3,4,6-tetrafluoro-5-methoxyphenyl) cyclohexane (6b), and 36 mg (13%) of (2,3,5,6-tetrafluoro-4-methoxyphenyl) cyclohexane (6c) were isolated.

Spectroscopic data of (2,3,4,5-tetrafluoro-6-methoxyphenyl) cyclohexane (6a):
^{19}F nmr spectrum: δ= -147 (1F, dd, J= 24; 10.5Hz, F-5), -157.5 (1F, t, J= 24Hz, F-4), -159 (1F, dd, J= 24; 10.5Hz, F-2), -165.8 ppm (1F, t, J= 24Hz, F-3); ^{1}H nmr (CCl$_4$): δ= 3.94 (3H, s, -OCH$_3$), 2.97 (1H, m, cyclohexyl H), 1.12-2.36 ppm (10H, m, -CH$_2$-); mass spectrum calcd. for $C_{13}F_4H_{14}O$ m/z 262.0981, found m/z 262.1002, m/z 262 (M$^+$, 40%), 206(20), 193(20), 182(70),

84(20), 82(20).

Spectroscopic data of (2,3,4,6-tetrafluoro-5-methoxyphenyl) cyclohexane (6b):
^{19}F nmr spectrum: δ= -139.5 (1F, d, J= 9Hz, F-6), -147 (1F, d, J= 24Hz, F-4), -156 (1F, d, J= 24Hz, F-2), -166.5 ppm (1F, td, J= 24; 9Hz, F-3); ^1H nmr (CCl_4): δ= 3.97 (3H, s, $-OCH_3$), 2.97 (1H, m, cyclohexyl H), 1.18-2.02 ppm (10H, m, $-CH_2-$); mass spectrum calcd. for $C_{13}F_4H_{14}O$ m/z 262.0981, found m/z 262.1002, m/z 262 (M^+, 100%), 216(74), 182(52).

Spectroscopic data of (2,3,5,6-tetrafluoro-4-methoxyphenyl) cyclohexane (6c):
^{19}F nmr spectrum: δ= -147.75 (2F, dd, J=24; 9Hz, F-3, F-5), -161.25 ppm (2F, dd, J= 24; 9Hz, F-2, F-6); ^1H nmr (CCl_4): δ= 4.06 (3H, s, $-OCH_3$), 2.97 (1H, m, cyclohexyl H), 1.24-2.03 ppm (10H, m, $-CH_2-$); mass spectrum calcd. for $C_{13}H_{14}F_4O$ m/z 262.0981, found m/z 262.0998, m/z 262(M^+, 14%), 261(100), 206(90), 193(50), 182(54).

Irradiation of Pentafluoroanisole in Methanol

The crude reaction mixture was separated by preparative glc (FFAP 30% on CHROM A/W at 210°C) and 31 mg (15%) of (2,3,4,5-tetrafluoro-6-methoxyphenyl) methanol (6a), 40 mg (19%) of (2,3,4,6-tetrafluoro-5-methoxyphenyl) methanol (6b), and 36 mg (17%) of (2,3,5,6-tetrafluoro-4-methoxyphenyl) methanol (6c) were isolated.

Spectroscopic data of (2,3,4,5-tetrafluoro-6-methoxyphenyl) methanol (6a):
^{19}F nmr spectrum: δ= -151.5 (1F, dd, J= 24; 10.5Hz, F-5), -162.7 (1F, t, J= 24Hz, F-4), -163.3 (1F, dd, J= 24; 10.5Hz, F-2), -170.2 ppm (1F, t, J= 24Hz, F-3); ^1H nmr (CCl_4): δ= 4.66 (2H, s, $-CH_2-$), 4.03 (3H, s, $-OCH_3$), 2.57 ppm (1H, broad singlet, -OH); mass spectrum calcd. for $C_8H_6F_4O_2$ m/z 210.0304, found m/z 210.0300, m/z 212(M^++2, 11%), 210(M^+, 18), 182(75), 167(100), 51(64).

Spectroscopic data of (2,3,4,6-tetrafluoro-5-methoxyphenyl) methanol (6b):
^{19}F nmr spectrum: δ= -144,75 (1F, d, J= 10.5Hz, F-6), -152.25 (1F, d, J= 24Hz, F-4), -156.0 (1F, d, J= 24Hz, F-2), -170.25 ppm (1F, td, J= 24; 10.5Hz, F-3); ^1H nmr (CCl_4): δ= 4.73 (2H, s, $-CH_2-$), 4.03 (3H, s, $-OCH_3$), 2.66 ppm (1H, broad singlet, -OH); mass spectrum calcd. for $C_8H_6F_4O_2$ m/z 210.0304, found m/z 210.0310, m/z 210(M^+, 59%), 193(38), 188(21), 181(55), 167(100), 165(34), 51(48).

Spectroscopic data of (2,3,5,6-tetrafluoro-4-methoxyphenyl) methanol (6c): ^{19}F nmr spectrum: δ= -152.25 (2F, dd, J= 24; 10.5Hz, F-3, F-5), -164.25 ppm (2F, dd, J= 24; 10.5Hz, F-2, F-6); ^{1}H nmr (CCl_4): δ= 4.7 (2H, s; $-CH_2-$), 4.09 (3H, s, OCH_3), 3.3 ppm (1H, broad singlet, -OH); mass spectrum calcd. for $C_8H_6F_4O_2$ m/z 210.0304, found m/z 210.0306, m/z 210(M^+, 100%), 182(62), 168(79), 52(54).

Irradiation of Pentafluoronitrobenzene in Cyclohexane

Separation of the crude reaction mixture was carried out by preparative glc (FFAP 30% on CHROM A/W at 220°C) and 62 mg (29%) of pentafluoronitrobenzene (7) and 29 mg (11%) of pentafluorophenyl cyclohexane (3a) (m.p. 43-44°C) were obtained. Spectroscopic data of pentafluorophenyl cyclohexane correspond to those published previously.[11*]

Irradiation of Octafluoronaphthalene in Methanol

We tried to separate the crude reaction mixture by preparative tlc (SiO_2, Al_2O_3, different mobile phases), preparative glc (different stationary phases).

^{19}F nmr spectrum of the mixture of isomers: δ_F= -117.75 (1F, dm), -118.5 (1F, dm), -145.5 (1F,tm), -146.25 (1F, tm), -147.75 (1F, tm), -148 (1F, tm), -150.75ppm (1F, tm), and -130.5 (1F, m), -132 (2F, m), -135.75 (1F, m), -139.5 (1F, ddm), -168.75 (1F, tm), -179.85 ppm (1F, tm).

Irradiation of Pentafluoropyridine in Methanol

The crude reaction mixture was separated by preparative glc (FFAP 30% on CHROM A/W at 180°C) and 85 mg (47%) of oily 2,3,5,6-tetrafluoro-4-(1-hydroxymethyl) pyridine (10a) was obtained.

Spectroscopic data:

^{19}F nmr spectrum: δ= -93.75 (2F, AA·XX· type of spectrum, F-2, F-6), -151.5 ppm (2F, AA·XX· type of spectrum, F-3, F-5); ^{1}H nmr (CCl_4): δ= 4.7 (2H, s, $-CH_2-$), 3.0 ppm (1H, broad singlet, -OH); mass spectrum calcd. for $C_6H_3F_4NO$ m/z 181.0151, found m/z 181.0147, m/z 181(M^+, 100%), 180(33), 164(37), 160(58), 151(28), 143(52), 142(47), 121(37), 100(28), 86(20), 84(23), 82(38), 75(22), 69(28).

Irradiation of Pentafluoropyridine in Ethanol

After separation by preparative glc (FFAP 30% on CHROM A/W at 190°C), 76 mg (39%) of oily 2,3,5,6-tetrafluoro-4-(1-hydroxyethyl) pyridine (10b) was isolated.

Spectroscopic data:

^{19}F nmr spectrum: δ= -91.4 (2F, AA'XX' type of spectrum, F-2, F-6), -147.8 ppm (2F, AA'XX' type of spectrum, F-3, F-5); ^1H nmr (CCl_4): δ= 5.2 (1H, q, J= 6Hz, -CH), 3.12 (1H, broad singlet, -OH), 1.64 ppm (3H, d, J= 6Hz, $-CH_3$); mass spectrum calcd. for $C_7H_5F_4NO$ m/z 195.0331, found m/z 195.0307, m/z 195(M^+, 22%), 181(10), 180(100), 132(25), 82(12).

Irradiation of Pentafluoropyridine in 1-Propanol

Separation was carried out by preparative glc (FFAP 30% on CHROM A/W at 195°C) and 98 mg (47%) of oily 2,3,5,6-tetrafluoro-4-(1-hydroxypropyl) pyridine (10c) was obtained.

Spectroscopic data:

^{19}F nmr spectrum: δ= -91.4 (2F, AA'XX' type of spectrum, F-2, F-6), -146 ppm (2F, AA'XX' type of spectrum, F-3, F-5); ^1H nmr (CCl_4): δ= 4.95 (1H, t, J= 6Hz, -CH), 3.27 (1H, broad singlet, -OH), 1.91 (2H, m, $-CH_2-$), 1.0 ppm (3H, t, J= 6Hz, $-CH_3$); mass spectrum calcd. for $C_8H_7F_4NO$ m/z 209.0464, found m/z 209.0466, m/z 209(M^+, 18%), 181(13), 180(100), 132(20), 121(10), 82(15).

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