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Studies on Organic Fluorine Compounds. XII.[1] Photolysis of (Fluoroalkyl)-*s*-triazines[2]

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Conjugated heterocyclic compound of low aromaticity, *s*-triazines (I) with CF_3 and/or CF_2Cl group, were irradiated and dihydro compounds (II), adducts (III), and substituted compounds (IV) were obtained. Ratio of II, III, and IV depended on the kind of the substituent present and the solvents working as reagent. Mechanism of these reactions was proposed from considering their effects.

Of various fluorinated polyazines, detailed studies have been made on the photochemical reaction of fluorodiazines,[4] but the photochemistry of (fluoroalkyl)-*s*-triazines is practically unknown. In order to examine the effect of fluorine on the photochemical reactivity of (fluoroalkyl)-*s*-triazines, we examined the reaction of [trifluoro (and/or chlorodifluoro)methyl]-*s*-triazines (Ia—d) under photoirradiation.

Result and Discussion

About 10% solution of [trifluoro (and/or chlorodifluoro)methyl]-*s*-triazine (Ia—d) in pentane and/or cylohexane was sealed in a quartz tube under reduced pressure and irradiated by a low-pressure mercury lamp for about 30 hr. The products thereby formed are listed in Table I with their yields.

The main products consisted of dihydro compounds (II), adducts (III), and/or substitution compounds (IV), and the product ratio depended on the kind of the substituent (R) present in I and the solvent used. In the case of Ia ($R_1=R_2=R_3=CF_3$), the dihydro compound and adducts were formed. In the case of Ib to Id, in which one or more CF_2Cl groups were present as substituents and the other substituents were CF_3 groups, the main products were the dihydro compounds and adducts when pentane was used as the solvent, while the substitution compound and adducts were formed as the main products, with a small amount of the dihydro compound, when cyclohexane was used as the solvent. In general, *s*-triazines have a strong absorption in the ultraviolet (UV) range of 280 nm and this absorption is said to be due to the n–π^* transition.[5] The reaction progresses when I is irradiated with a low-pressure mercury lamp in a quartz tube (2537 Å) but not with a high-pressure lamp in a Pyrex tube (3650 Å) and the starting material is recovered. The starting material is also recovered when the reaction is carried out without a solvent (in the gas or liquid phase), or when perfluoropentane is used as the solvent, or when *ca.* 10% piperylene is added as a quencher. These facts suggest that this is a radical reaction probably induced by the n–π^* excitation.

1) Part XI: Y. Kobayashi, I. Kumadaki, A. Ohsawa, and M. Honda, *Chem. Pharm. Bull.* (Tokyo), **21**, 867 (1973).
2) Presented at the 92nd Annual Meeting of the Pharmaceutical Society of Japan, Osaka, April 1972.
3) Location: *Kitashinjuku 3-chome, Shinjuku-ku, Tokyo.*
4) *a*) C.G. Allison, R.D. Chambers, J.A.H. McBride, and W.K.R. Musgrave, *Chem. Commun.*, **1969** 1201 *idem*, *J. Chem. Soc.* (*C*), **1970** 1023 *b*) D.W. Johnson, V. Austel, R.S. Feld, and D.M. Lemal, *J. Am. Chem. Soc.*, **92**, 7505 (1970).
5) E.S. Stern and C.J. Timmons, "Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold, Ltd., London, 1970.

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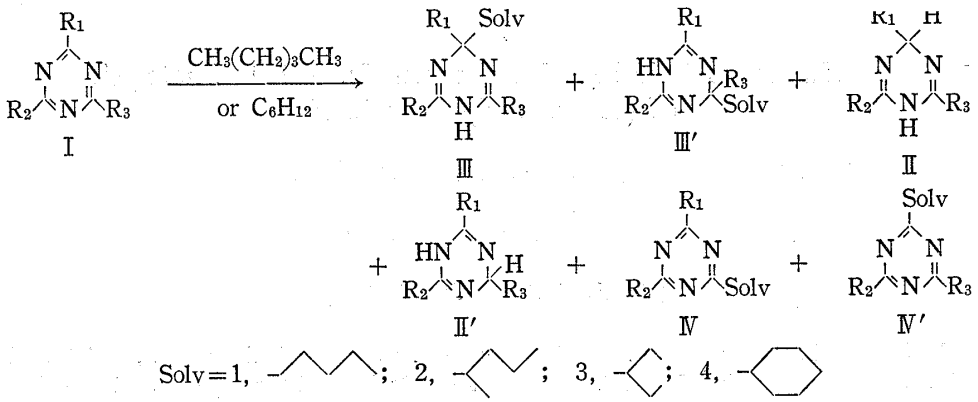
Table I. Yield by Photolysis (%)



	I				In *n*-Pentane III-			In *n*-Pentane III'-					IV-	IV'-
	R_1	R_2	R_3	I	1	2 (or 3)	3 (or 2)	1	2 (or 3)	3 (or 2)	II	II'	1-3	1-3
a	CF_3	CF_3	CF_3	19[a]	8[b]	12[c]	25[c]	—	—	—	32[d]	—	—	—
b	CF_3	CF_3	CF_2Cl	~2[a]	5.5[b]	7.5[c]	15[c]	1.5[e]	5.5[e]		27[f]	27[f]	~5[e]	0
c	CF_3	CF_2Cl	CF_2Cl	~5[a]	2[e]	5[c]	14[c]	2[e]	6[c]	13[c]	13[f]	13[f]	~2[e]	0
d	CF_2Cl	CF_2Cl	CF_2Cl	~4[a]	—	—	—	3[b]	9[c]	27[c]	—	36[d]	~7[e]	0

	In cyclohexane						
	I	III-4	III'-4	II	II'	IV-4	IV'-4
a	trace[a]	71[g]	—	25[d]	—	—	—
b	trace[a]	55[b]	6[b]	3.5[f]	3.5[f]	24[g]	0
c	trace[a]	20[b]	20[b]	trace[f]	trace[f]	54[g]	0
d	trace[a]	—	40[b]	rtace[f]	trace[f]	52[g]	0

a) Products identified and determined by gas chromatography.
b) Products isolated as oil by preparative gas chromatography.
c) Products obtained as oily mixture by preparative gas chromatography and composition ratio determined by ^{19}F-NMR spectrum.
d) The product isolated as crystals by silica gel chromatography.
e) Products presumed and determined by gas chromatographic mass spectrum and gas chromatography.
f) The product obtained as a solid mixture by silica gel chromatography and composition ratio determined by derivation to III or III', and by ^{19}F-NMR spectra.
g) Products isolated as oil by silica gel chromatography.

The characteristic feature of this reaction is that the substitution dose not occur on the ring carbon attached to CF_3 group either in pentane or in cyclohexane, but only hydrogenation and solvent addition occur. In contrast, substitution occurs on a small scale, in addition to hydrogenation and solvent addition on the ring carbon attached to CF_2Cl group when pentane is used as the solvent, and substitution and solvent addition take place preferentially over hydrogenation when cyclohexane is used. These facts can be exp lained qualitatively by the following hypothesis: (a) There is a difference in the carbon-carbon bond energy between the C-CF_3 and C-CF_2Cl groups, due either to the difference in electronegativities of fluorine and chlorine, or to the difference between inverse hyperconjugation effects of CF_3 and CF_2Cl groups. This results in difference in the ease of radical fission of the carbon-carbon bond. (b) The reaction between the radical formed by this fission and the solvent in a certain mechanism (or the solvent radical) progresses smoothly in cyclohexane but not so smoothly in pentane. These hypotheses may be supported indirectly by the fact that chlorodifluoromethane ($M^+-1=85$) was detected by mass spectroscopy from the gas evolved during the reaction in the vessel after irradiation of Ib in cyclohexane but fluoroform was not.

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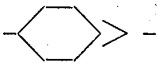
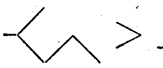
From the yield of adducts given in Table I, it is known that the ease of addition decreased in the order of  or  . This became more apparent by irradiation of Ia in an equimolar mixture of cyclohexane and pentane, from which IIIa-1, IIIa-2 (or IIIa-3), IIIa-3 (or IIIa-2), and IIIa-4 were formed in approximate ratio of 0.5:1:2:10. While the substitution compound (IVb-d) is obtained in a considerable yield in cyclohexane, it is obtained only in a trace in pentane. These facts can be explained by assuming that the ratio of products formed is controlled by the stability of the alkyl radical (Chart 1).

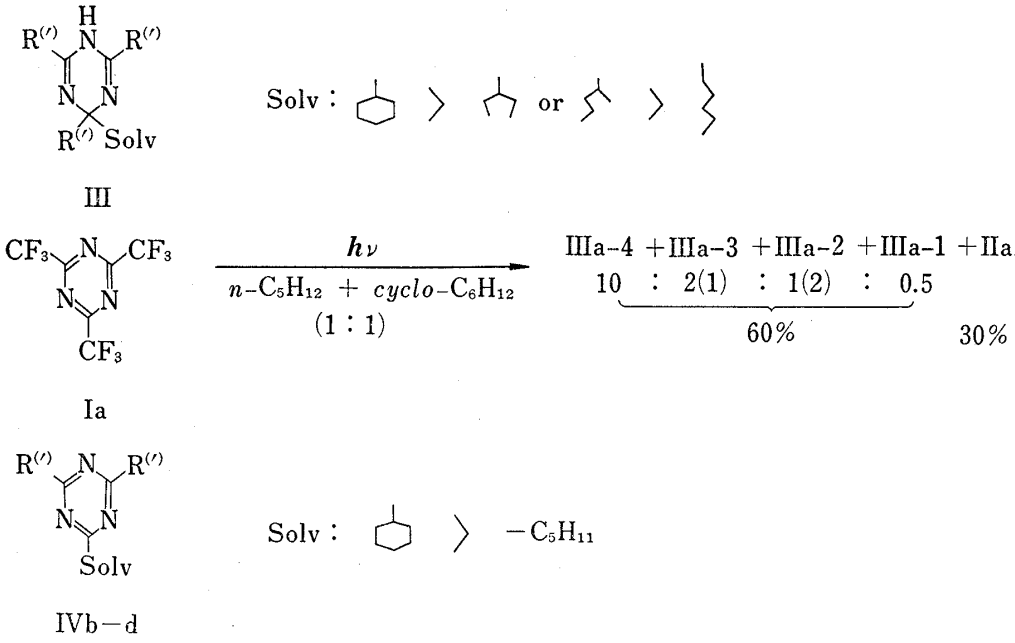


Chart 1

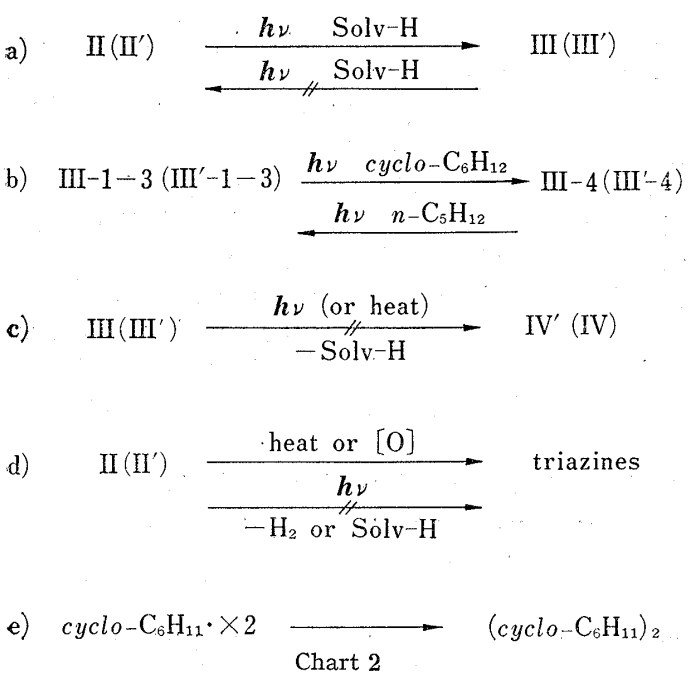


Chart 2

Further, in order to clarify the formation of II, III, and IV, the following experiment was carried out (Chart 2). (a) Further irradiation of II gives the corresponding III but irradiation of III dose not give the corresponding II. (b) Irradiation of III in a different solvent results in the exchange of addition group with the solvent. (c) Irradiation of III does not afford the corresponding IV, but III is recovered. (Consequently, the substitution compound (IV) is not formed from the adduct (III) by the elimination of HCF_2Cl but must be formed by a different route). (d) Irradiation of II does not result in the formation of *s*-triazines by dehydrogenation or elimination of RH, although II undergoes dehy-

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drogenation on being heated or treated with an oxidizing agent.[6] (e) Gas chromatographic mass spectrum of the reaction mixture given in cyclohexane indicates the presence of biscyclohexane, suggesting the formation of a solvent radical.

From the foregoing facts, it can be understood that this reaction is controlled by the following factors: (a) ease of n–π^* excitation, (b) ease of homolitic fission between the carbon atom in *s*-triazine ring and the substituent, R, (c) quantity of the solvent working as a reagent and population of the solvent radical due to the stability, and (d) stability of the monoradical and biradical of *s*-triazine. The mechanism of this reaction can be proposed as shown in Chart 3 by considering the above factors that control this reaction.

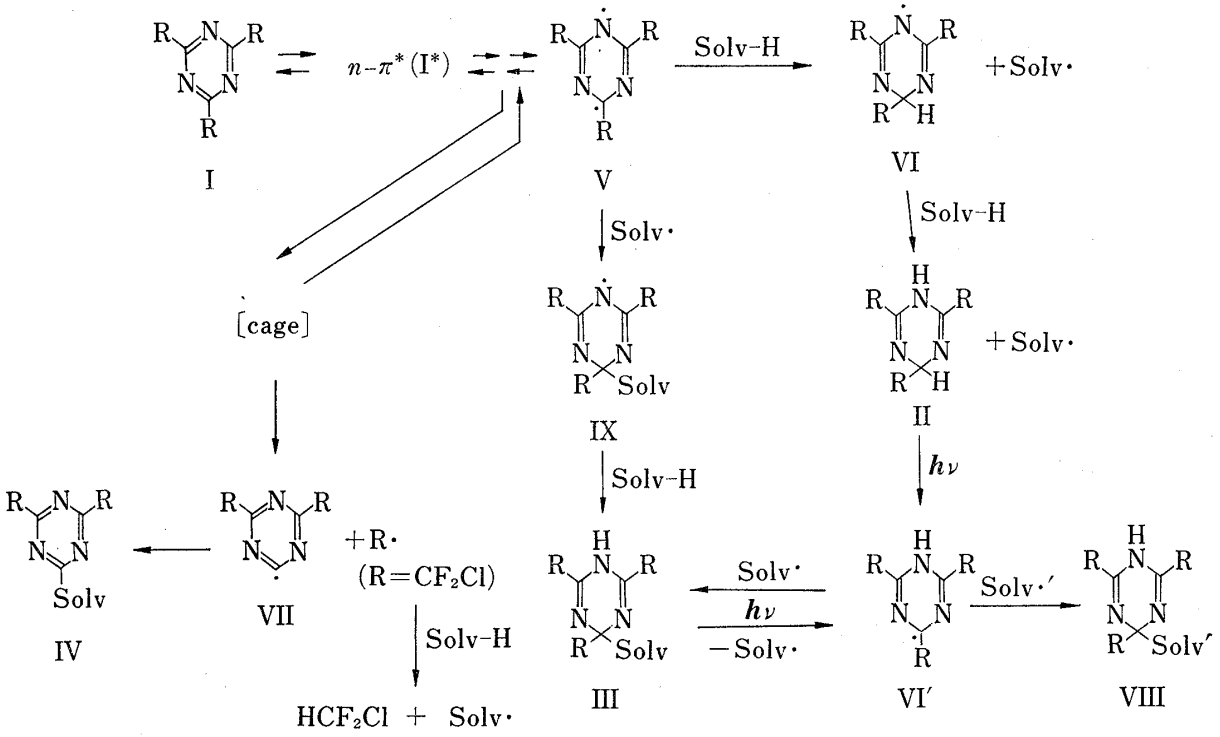


Chart 3

The biradical (V) is first formed *via* n–π^* excitation of I and this biradical extracts a proton from the solvent molecule, forming the radical (VI) which further extracts a proton from the solvent molecule to form the dihydro compound (II). II is photochemically excited to produce the radical (VI′) which combines with the solvent radical to produce the adduct (III). Formation of III by another route through IX from V and the solvent radical cannot be denied at present. Exchange of the introduced solvent moiety (Solv) with the solvent molecule (Solv′-H) may be explained by the route of III→VI′→VIII. In addition, when I carried CF_2Cl group as a substituent, monoradical (VII) is also formed by the fission of carbon-carbon bond in V and a substitution compound (IV) is produced by the bonding of VII and the solvent radical. Since the product ratio of IV to III+II is dependent on the stability of the solvent radical, it may be assumed that the radical VII and CF_2Cl radical form a cage,[7] which is in an equilibrium with V.

Separation, Estimation, and Establishment of the Structure of Reaction Products

While II are solids, III and IV are volatile oils and their separation was effected by column chromatography over silica gel and preparative gas chromatography. The yield of

6) This contrasts with the conversion of 1,2-dihydro-2,4,6-triphenyl-*s*-triazine to 2,4,6-triphenyl-*s*-triazine by photo-dehydrogenation reported by Nyquist (H.L. Nyquist, *J. Org. Chem.*, 31, 784 (1966)).
7) H. Shizuka, T. Kanai, T. Morita, Y. Ohno, and K. Matsui, *Tetrahedron*, 27, 4021 (1971).

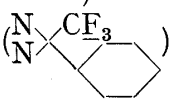
NII-Electronic Library Service

products in Table I was calculated from the weight of substances separated by column chromatography, ratio of peak area in gas chromatography, and for some of the mixtures, from the intensity ratio of absorptions in ^{19}F-nulcear magnetic resonance (^{19}F-NMR) spectra.

Irradiation of Ia in pentane afforded a crystalline product (IIa) of mp 173—175° and an oil separated by column chromatography. Mass spectrum of IIa showed M^+ at *m/e* 287 and its infrared (IR) spectrum (in $CHCl_3$) showed characteristic absorptions at 3400 (ν_{N-H}), 1740 ($\nu_{N=C}$), and 1160 (ν_{C-F}) cm^{-1}.

The ^{19}F-NMR of IIa (in MeOH) exhibited absorptions at 12.0 (2 N=$\langle{}^{CF_3}_{N}$) and 12.3 ($^{N}_{N}\!\!\times{}^{CF_3}_{H}$) ppm[8,9] with intensity ratio of 2:1. The gas chromatogram of the foregoing oil showed three peaks which were separated using preparative gas chromatography. The first fraction was identified with Ia by gas chromatography, mass spectrum and IR spectrum. The mass spectrum of the third fraction exhibited M^+ at *m/e* 357, its IR spectrum (in $CHCl_3$) showed absorptions at 3380 (ν_{N-H}), 2950 (ν_{C-H}), 1740 ($\nu_{C=N}$), and 1160 (ν_{C-F}) cm^{-1}, and its ^{1}H-NMR spectrum (in $CDCl_3$) showed absorptions at δ: *ca.* 8 (broad singlet, 2/3 N$\underline{H}$), *ca.* 6 (broad singlet, 1/3 N$\underline{H}$),[10] 2 (multiplet, 2 H, $^{N}_{N}\!\!\times{}^{C\underline{H}_2^-}_{CF_3}$), 1.3 (multiplet, 6 H), and 0.9 (multiplet, 3 H, C$\underline{H}_3$), while its ^{19}FNMR (in MeOH) had absorptions at 12.3 (2 N=$\langle{}^{CF_3}_{N}$) and 22.8 ($^{N}_{N}\!\!\times{}^{CF_3}$) ppm. These data show that this fraction is IIIa-1.

IR spectrum (in $CHCl_3$) of the second fraction was very similar to that of IIIa-1, having absorptions at 3380, 2950, 1740, and 1160 cm^{-1}. ^{1}H-NMR of this fraction exhibited absorptions at δ: *ca.* 8 (broad singlet, 2/3 N$\underline{H}$), *ca.* 6 (broad singlet, 1/3 N$\underline{H}$), 2.2 (multiplet, *ca.* 5 H). From similarity of the IR spectrum to those of IIIa-1, ^{1}H-NMR spectrum, and the fact that retention time of gas chromatography is shorter than that of IIIa-1 (See experimental parts (a) and (e)), it is supposed that this fraction consisted of IIIa-2 and IIIa-3. In addition, the largest ion (*m/e* 357) and fragment pattern in the mass spectrum of this fraction agreed with those of IIIa-2 and/or IIIa-3. Its ^{19}F-NMR (in MeOH) had signals at 12.1 (N=$\langle{}^{CF_3}_{N}$), 12.2 (N=$\langle{}^{CF_3}_{N}$), 16.5 ($^{N}_{N}\!\!\times{}^{CF_3}_{solv}$), and 17.0 ($^{N}_{N}\!\!\times{}^{CF_3}_{solv}$) ppm in intensity ratio of 2:1:1:0.5. On the foregoing supposition and from this signal ratio, it is shown that this fraction should be a 1:2 or 2:1 mixture of IIIa-2 and IIIa-3.

Irradiation of Ia in cyclohexane afforded IIa and an oily product (IIIa-4), which were separated by silica gel chromatography. Mass spectrum of IIIa-4 showed M^+ at *m/e* 369, its IR spectrum (in $CHCl_3$) being similar to that of IIIa-1, exhibiting absorptions at 3390 (ν_{N-H}), 2940 (ν_{C-H}), 1740 ($\nu_{C=N}$), and 1150 (ν_{C-F}) cm^{-1}. The ^{1}H-NMR of IIIa-4 (in $CDCl_3$) had signals at δ: *ca.* 8 (broad singlet, 2/3 N$\underline{H}$), *ca.* 6 (broad singlet, 1/3 N$\underline{H}$), 2.2—1.5 (multiplet, *ca.* 6 H), and 1.2 (multiplet, *ca.* 5 H). The ^{19}F-NMR spectrum (in MeOH) showed absorptions at 12.1 (2 N=$\langle{}^{CF_3}_{N}$) and 16.4 ($^{N}_{N}\!\!\times{}^{CF_3}$ ) ppm with intensity ratio of 2:1. Separation, estimation, and structural determination data for the reaction products of Ib—d will be described in the experimental part.

Experimental

Apparatus

Light source (2537 Å) was an Ushio ULO-6AB lamp (6 W). Gas chromatograph was a Shimadzu Model GC-1C with 3 m column, packed with 15% diethylene glycol succinate. Gas chromatographic mass spectra

8) Benzotrifluoride = 0 ppm (as internal standard).
9) Detailed examination on the ^{19}F-NMR of these compounds will be reported in a separate paper.
10) The ^{19}F-NMR indicated that III contains 1,4-(N$\underline{H}$, δ: *ca.* 8) and 1,2-(N$\underline{H}$, δ: *ca.* 6) dihydro types.[9]

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were measured with Hitachi Model K 53 (GC), RM-7L (MS), with a packing of 15% diethylene glycol succinate.

(a) **Irradiation of Ia in Pentane**——A pentane solution containing 0.8 g of Ia (10%) was filled in a quartz ampule, sealed *in vacuo*, and irradiated for 30 hr, by which a colorless precipitate appeared on the ampule wall. The ampule was opened, the reaction mixture was washed out with ether, and the solvent was evaporated at room temperature by the use of a vacuum line. The residue was submitted to column chromatography over silica gel and the effluent obtained by elution with ether–pentane afforded 0.58 g of an oil. This oil showed three peaks in gas chromatography (150°, 1 atm), with retention time of 3, 6.5, and 9 min, respectively. These fractions were separated using preparative gas chromatography. The peak with retention time of 3 min agreed with Ia. Recovery, 19%. The ratio of peak areas with retention time of 6.5 and 9.0 min was 5: 1. The peak with retention time of 6.5 min was a volatile oil with the following physical data: IR (in $CHCl_3$) cm^{-1}: 3380, 2950, 1740, 1680, 1160. ^{1}H-NMR (in $CDCl_3$) δ: *ca.* 8 (broad singlet, 2/3 H), *ca.* 6 (broad singlet, 1/3 H), 2.2 (multiplet, 1 H), 1.6—1.3 (*ca.* 5H), 1.0 (*ca.* 5H). ^{19}F-NMR (in MeOH) ppm: 12.1, 12.2, 16.5, 17.0. Intensity ratio: 2: 1: 1: 0.5 (IIIa-2: IIIa-3=1: 2 or 2: 1). The fraction with retention time of 9.0 min was also a volatile oil (IIIa-1) with the following physical data: IR (in $CHCl_3$) cm^{-1}: 3380, 2950, 1740, 1680, 1160. ^{1}H-NMR (in $CDCl_3$) δ: *ca.* 8 (broad singlet, 2/3H), *ca.* 6 (broad singlet, 1/3H), 2 (multipelt, 2H), 1.3 (multiplet, 6H), 0.9 (multiplet, 3H). ^{19}F-NMR (in MeOH) ppm: 12.3, 22.8. Intensity ratio: 2: 1.

The ether eluate from the silica gel chromatographic column afforded 0.26 g of IIa as sublimable prisms (from benzene–hexane), with a melting point at 173—175°. *Anal.* Calcd. for $C_6H_2N_3F_9$: C, 25.08; H, 0.69; N, 14.63; F, 59.58. Found: C, 25.38; H, 1.11; N, 14.99; F, 59.68. IR (in $CHCl_3$) cm^{-1}: 3400, 1740, 1680, 1160. ^{19}F-NMR (in MeOH) ppm: 12.0, 12.3. Intensity ratio: 2: 1. Mass Spectrum *m/e*: 287 (M^+).

(b) **Irradiation of Ia in Cyclohexane**——A cyclohexane solution containing 0.66 g of Ia (10%) was irradiated in the same way as in (a). After the reaction mixture was treated as in (a), the residue was submitted to column chromatography over silica gel, and 0.17 g of IIa and 0.61 g of IIIa-4 were obtained. IIIa-4 occurred as a volatile oil. Mass Spectrum *m/e*: 369 (M^+). IR (in $CHCl_3$) cm^{-1}: 3390, 2940, 1740, 1680, 1150. ^{1}H-NMR (in $CDCl_3$) δ: *ca.* 8 (broad singlet, 2/3H), *ca.* 6 (broad singlet, 1/3H), 2.2—1.5 (multiplet, *ca.* 6H), 1.2 (multiplet, *ca.* 5H). ^{19}F-NMR (in MeOH) ppm: 12.1, 16.4. Intensity ratio: 2: 1. From the irradiated solution, biscyclohexane was detected by gas chromatographic mass spectrum.

(c) **Irradiation of IIa in Pentane**——A suspension of 0.05 g of IIa in *ca.* 0.5 ml of pentane was irradiated as in (a) and the irradiated solution was submitted to gas chromatography. Two peaks were detected with area ratio of 5: 1. These peaks corresponded to those supposed to be of IIIa-2 + IIIa-3 and those of IIIa-1 found in (a) and the patterns of the gas chromatographic mass spectra of these substances were the same as those of the compounds detailed earlier. Ia was not detected.

(d) **Irradiation of IIa in Cyclohexane**——By the same treatment of 0.05 g of IIa as in (c), IIIa-4 was detected by gas chromatography but Ia was not.

(e) **Irradiation of Ib in Pentane**——A pentane solution containing 0.48 g of Ib (10%) was similarly irradiated. A precipitate was detected on the tube wall. After treatment as in (a), the residue was separated into fractions of pentane eluate, pentane–ether eluate, and ether eluate by column chromatography. The first fraction was concentrated at room temperature by the use of a vacuum line and three peaks were detected in its residue by gas chromatography (100°, 0.8 atm), with retention time of 5.5, 11.5, and 15 min. The first peak agreed with Ib, and both the second and third peaks showed the largest ion at *m/e* 287, suggesting that they are IVb-2 + IVb-3 and IVb-1. Their fragment pattern was not inconsistent with these structures. Their yield was calculated from the ratio of peak areas in gas chromatography.

The second fraction was treated in the same way as above and gave 0.21 g of an oil. Gas chromatography (138°, 0.8 atm) of this oil showed four peaks with retention time of 14, 15.5, 21, and 25 min, and area ratio of 20: 5: 5: 1. They all had the largest ion at *m/e* 373 in gas chromatographic mass spectra. The substances corresponding to the oil with the first and third retention time were able to be isolated. The oil of the first fraction showed ^{1}H-NMR signals like those supposed to be of IIIa-2 + IIIa-3. ^{19}F-NMR (in MeOH) ppm: 0.6 (N=⟨N^{CF_2Cl}), 0.7 (N=⟨N^{CF_2Cl}), 12.1 (N=⟨N^{CF_3}), 12.2 (N=⟨N^{CF_3}), 16.3 (N⟩N^{CF_3}, Solv), 16.8 (N⟩N^{CF_3}, Solv). Intensity ratio: 4: 2: 6: 3: 6: 3.

These data suggest that this fraction consisted of IIIb-2 and IIIb-3, their ratio being 1: 2 or 2: 1.

The IR (3380, 2950, 1735, 1680, 1165 cm^{-1} in $CHCl_3$) and ^{1}H-NMR spectra (δ: *ca.* 8; 2/3H, *ca.* 6; 1/3H, 2; 2H, 1.3; 6H, 0.9; 3H in $CDCl_3$) of the third fraction were similar to those of IIIa-1, while its ^{19}F-NMR spectrum exhibited signals at 0.8, 12.3, and 22.8 ppm (in MeOH) with intensity ratio of 2: 3: 3. Therefore, this fraction is IIIb-1, and the substances corresponding to the retention time of the second and fourth fractions would be III′b-3 + III′b-2 and III′b-1, respectively, from their gas chromatographic mass spectra and retention time of their gas chromatography.[11] The yield of IIIb-1 to -3 and III′b-1 to -3 was calculated from the area ratio in gas chromatography and intensity ratio of signals in ^{19}F-NMR spectra.

11) In general, retention time of type III compounds in DEGS column is III-2≃III-3<III-1<III-4, due to the size and form of substituents.

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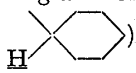
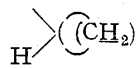
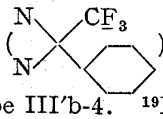
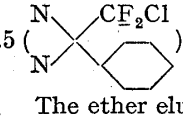
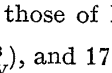
The ether eluate of the silica gel chromatographic column afforded 0.27 g of a sublimable solid melting at about 133° (not sharp). This was found to be an approximately equimolar mixture of IIb and II'b, with the largest ion at *m/e* 203. IR absorptions were very similar to those of IIa (3390, 1735, 1670, 1165 cm^{-1} in $CHCl_3$). ^{19}F-NMR (in MeOH) ppm: −0.5 ($C\underline{F}_2Cl$), 0.0 ($C\underline{F}_2Cl$), 11.7 ($C\underline{F}_3$). 12.0 ($C\underline{F}_3$), 12.3 ($C\underline{F}_3$), with intensity ratio 2: 2: 3: 6: 3. Irradiation of this solid in cyclohexane in the same way as in (d) and gas chromatography of the irradiated solution resulted in the detection of IIIb-4 and III'b-4 in approximately 1: 1 ratio. Recrystallization of IIb and II'b was attempted in various solvents but their separation was not effected.

(f) **Irradiation of Ib in Cyclohexane**——After irradiation of cyclohexane solution containing 0.52 g of Ib (10%), in the same way as in other cases, the gas phase inside the ampule was collected by a sampler. Mass spectrum of this gas showed the base peak at *m/e* 85, which was considered to be due to $M^+ - 1$ of CF_2-ClH from its fragment pattern. CF_3H or CF_3 (*m/e* 70 or 69) was not detected. The solution from the ampule was treated in the same way as described in (e), and pentane eluate (0.12 g), pentane–ether eluate (0.40 g), and ether eluate (0.04 g) were obtained. The pentane eluate afforded a volatile oil (IVb-4) whose mass spectrum exhibited M^+ at *m/e* 299, not containing a chlorine atom.

^{1}H-NMR (in $CDCl_3$) δ: 3.1 (multiplet, 1H, ), 2.4—1.0 (multiplet, 10H, ), ^{19}F-NMR (in $CDCl_3$) ppm: 10.0.

The pentane–ether eluate also afforded a volatile oil whose gas chromatogram showed two peaks, with retention time (at 160°, 1 atm) of 6.5 and 7.1 min, respectively. Gas chromatographic mass spectrum exhibited M^+ at *m/e* 385 for both, with area ratio of 10: 1. Fractions corresponding to these two peaks were separated by preparative gas chromatography. The oil with retention time of 6.5 min was found to be IIIb-4. ^{19}F-NMR (in MeOH) ppm: 0.75 (N=), 12.2 (N=), 16.4 (), with intensity ratio of 2: 3: 3. The oil with retention time of 7.1 min was found to be III'b-4. ^{19}F-NMR (in MeOH) ppm: 0.5 (), 12.0 (2N=), with intensity ratio of 1: 3.

The ether eluate afforded a solid which was found to have the same composition as the solid described in (e), and their ratio was approximately 1: 1 (by ^{19}F-NMR).

(g) **Irradiation of Ic in Pentane**——After irradiation of pentane solution containing 0.60 g of Ic (10%) and treatment as in (e), gas chromatography and its mass spectrum of the pentane eluted fraction of the silica gel chromatographic column showed the presence of 5% of Ic, IVc-2 + IVc-3, and IVc-1 (with a total of 2%, the largest ion at *m/e* 303). Pentane–ether eluate afforded 0.31 g of an oil whose gas chromatography (150°, 0.8 atm) showed peaks with retention time of 12.5, 13.5, 17.5, and 21.5 min, and all had the largest ion at *m/e* 389, with area ratio of 10: 10: 1: 1. The fractions corresponding to the first and second peaks were isolated by preparative gas chromatography. Both were oils and their IR (3380, 2950, 1735, 1680, 1165 cm^{-1} in $CHCl_3$) and ^{1}H-NMR (δ: *ca.* 8; 2/3H, *ca.* 6; 1/3H, 2.2 1H, 1.6—1.3; *ca.* 5H, 1; *ca.* 5H in $CDCl_3$) spectra were quite similar to those of IIIa-2 + IIIa-3. ^{19}F-NMR (in MeOH) of the first fraction, ppm: 0.7 (N= ), 16.3 ( ), and 17 ( ), with intensity ratio of 16: 9: 3, suggesting this mixture is a 1: 3 or 3: 1 one of IIIc-2 and IIIc-3.

^{19}F-NMR (in MeOH) of the second fraction, ppm: 0.7 ($C\underline{F}_2Cl$), 1.3 (CF_2Cl), 12.2 ( ), and 12.3 ( ), with intensity ratio of 6: 6: 6: 3. This shows that this fraction is a 1: 2 or 2: 1 mixture of III'c-2 and III'c-3. The remaining third and fourth peaks correspond respectively to IIIc-1 and III'c-1.

The ether eluate from the silica gel column afforded a solid melting at *ca.* 104° (not sharp), in 0.15 g yield. Its M^+ was present at *m/e* 319 and its IR spectrum (3390, 1735, 1670, 1165 cm^{-1} in $CHCl_3$) was quite similar to that of IIa, while its ^{19}F-NMR spectrum (in MeOH) had signals at (ppm) −1.0 ($C\underline{F}_2Cl$), 0.0 ($C\underline{F}_2Cl$), 0.3 ($C\underline{F}_2Cl$), 12.0 (N=) and 12.1 ( ), with intensity ratio of 2: 2:4: 3: 3. The solution obtained by irradiation of this solid in cyclohexane in the same way as in (d) contained IIIc-4 and III'c-4 in approximately 1: 1 ratio, as revealed by gas chromatography. It follows, therefore, that the foregoing solid is an equimolar mixture of IIc and II'c, but their separation by recrystallization was unsuccessful.

(h) **Irradiation of Ic in Cyclohexane**——Ic was irradiated in the same way as in (f), and separation through column chromatography and preparative gas chromatography afforded IVc-4, IIIc-4, III'c-4, and a trace of IIc+II'c. IVc-4: ^{1}H-NMR (in $CDCl_3$) δ: 3.1 (multiplet, 1H), 2.4—1.0 (multiplet, 10H). ^{19}F-NMR (in MeOH) ppm: −1.4 (2F, $C\underline{F}_2Cl$), 10.0 (3F, $C\underline{F}_3$). IIIc-4: ^{19}F-NMR (in MeOH) ppm: 0.6 (4F, 2N=), 16.5 (3F,). Mass Spectrum *m/e*: 401 (M^+). III'c-4: ^{19}F-NMR (in MeOH), ppm: 0.7 (2F, $C\underline{F}_2Cl$), 1.3 (2F, $C\underline{F}_2Cl$), 12.1 (3F, $C\underline{F}_3$). Mass Spectrum *m/e*: 401 (M^+).

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(i) **Irradiation of Id in Pentane**——Id was irradiated in the same way as in (e) and (g), and the products were quantitatively examined. II'd, III'd-2+III'd-3, III'd-1, and a mixture of IVd-1—3 were obtained. II'd was obtained as sublimable prisms, mp *ca.* 100° (from benzene–hexane), with M^+ at *m/e* 335. IR (in $CHCl_3$), cm^{-1}: 3390, 1735, 1670, 1165. *Anal.* Calcd. for $C_6H_2N_3Cl_3F_6$: C, 21.49; H, 0.60.; N, 12.54; F, 34.03. Found: C, 21.31; H, 1.02; N, 12.00; F, 33.51. ^{19}F-NMR (in MeOH) ppm: −1.0 (2F, $\overset{N}{N}\!\times\!\overset{CF_2Cl}{H}$), 0.0 (4F, $2N{=}\langle^{CF_2Cl}_{N}$). III'd-2+III'd-3: Mass Spectrum: the largest ion at *m/e* 405. ^{19}F-NMR (in MeOH) ppm: 0.75, 0.8, 1.0. Intensity ratio: 3: 1: 8. III'd-1: Mass Spectrum *m/e*: 405 (M^+). ^{19}F-NMR (in MeOH) ppm: 1.0, 1.0 (broad).

(j) **Irradiation of Id in Cyclohexane**——Id was irradiated and treated as in (f) and (h). Column chromatography over silica gel afforded III'd-4 and IVd-4. III'd-4: mass spectrum *m/e*: 417 (M^+). ^{19}F-NMR (in MeOH), ppm: 0.6 ($C\underline{F}_2Cl$), 0.7 (broad, 2 $C\underline{F}_2Cl$). IVd-4: Mass Spectrum *m/e*: 331 (M^+). ^{19}F-NMR (in MeOH), ppm: −1.5 (2 CF_2Cl).

(k) **Irradiation of Ia—d with Light of 3650 Å**——Irradition was done in the same way as in the foregoing (a) to (j), using a high-pressure mercury lamp (Ushio UM-102), of 100 W, 3650 Å.

(l) **Quenching of Irradiation of Ia—d by Piperylene**——Ia—d were irradiated in cylohexane in the same manner as in (a) to (j), in the presence of piperylene (*ca.* 10% concentration).

(m) **Irradiation of Ia—d with Light of 2537 Å without Solvent**——Ia—d were placed in a silica flask, chilled in dry ice acetone, degassed to 0.5 Torr, and irradiated at room temperature. Under these conditions, all the compounds showed slight coloration at flask wall, and only the starting materials were detected by gas chromatography, recovery rate being over 90%.

(n) **Irradiation of Ia in Pentane-Cyclohexane Mixture**——Ia was treated in the same way as in (a) and (b), with 7: 8 mixture of pentane and cyclohexane. The crystalline product obtained was IIa, and the oily product was found to be a 10: 2: 1: 0.5 mixture of IIIa-4, IIIa-3 or IIIa-2, and IIIa-1 from the result of gas chromatography and ^{19}F-NMR spectrum.

(o) **Irradiation of III and III'**——IIIa-4 was irradiated in pentane by the usual method and gas chromatographic examination revealed the presence of IIIa-1 and IIIa-2+IIIa-3 in area ratio of 1: 5. IIa, Ia, or other products were not detected. Irradiation of III'd-1 in cyclohexane afforded III'd-4 in more than 90% yield as detected by gas chromatography, without the presence of IVd-4 or any other products.

(p) **Dehydrogenation of IIa with $Pb(AcO)_4$**——$Pb(AcO)_4$ was added to the ether solution of IIa under ice cooling, the mixture was allowed to stand for 30 min, and ether layer was washed with water and dehydrated with Na_2SO_4. From this solution Ia was detected as the product by gas chromatography.

(q) **Pyrolysis of II**——IId was sealed in a glass capillary and allowed to stand in H_2SO_4 bath of 150° for 5 min. Gas chromatography of the capillary content showed the presence of Id.

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