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SYNTHESES OF FLUORINE-CONTAINING FUSED POLYCYCLIC COMPOUNDS :
PHOTO-CYCLOADDITION OF INDENE TO CYCLIC FLUORO-OLEFINS AND
SOME REACTIONS CONCERNING THE ADDUCTS

HIROSHI KIMOTO, HIROSHIGE MURAMATSU and KAN INUKAI

Government Industrial Research Institute, Nagoya ;
Hirate-machi, Kita-ku, Nagoya 462 (Japan)

SUMMARY

Acetophenone photo-sensitized addition of indene to cyclic fluoro-olefins (1,2-dichlorohexafluorocyclopentene-1, 1,2-dichlorotetrafluorocyclobutene-1 and hexafluorocyclobutene) gave the corresponding cycloadducts in satisfactory yields. The cycloadducts obtained predominantly had *exo* configuration.

Some reactions such as reduction, oxidation, dechlorination and halogenation, of the cycloadducts were also studied.

INTRODUCTION

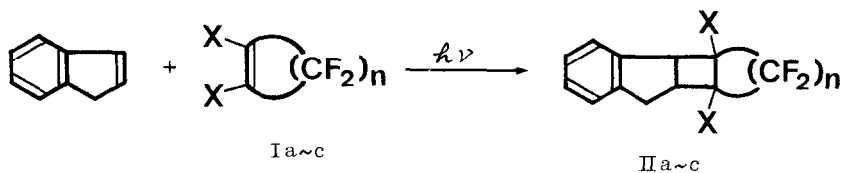
Thermal cycloaddition of fluoro-olefins has been studied rather extensively, but only a few investigations [1] on photo-cycloaddition of fluoro-olefins have been carried out. Since photo-cycloaddition is expected to have different scope from thermal reaction in the syntheses of cyclobutane derivatives, we examined the photo-cycloaddition of indene to some cyclic fluoro-olefins as a part of our studies [2] on synthetic aspects of addition reactions of fluoro-olefins.

In thermal reaction, it has been said [3] that the presence of a terminal difluoromethylene group is required for the fluoro-olefins to give cycloadducts in high yield and that symmetrically substituted ethylenes such as 1,2-dichloro-1,2-difluoroethylene do not undergo cycloaddition. Consequently, the cyclic fluoro-olefins employed in this investigation would not give cycloadducts thermally.

Ever since indene was found to give the head-to-head dimers under photo-irradiation [4], photo-sensitized cycloaddition of indene to several olefins have been reported. The yields were reported to be good in the cases of the olefins having an electron-withdrawing substituent such as chlorine [5], cyano [6] and carbonyl [7] groups. In this connection, it was interesting to examine the effect of fluorine, an electronegative substituent, on the photo-cycloaddition. Thus, we studied the photo-sensitized reaction of indene with cyclic fluoro-olefins (1,2-dichlorohexafluorocyclopentene-1, 1,2-dichlorotetrafluorocyclobutene-1 and hexafluorocyclobutene).

RESULTS AND DISCUSSION

Irradiation (>300 nm) of indene and an excess of fluoro-olefins (Ia~c) in the presence of acetophenone as a sensitizer gave the corresponding cycloadducts (IIa~c). The reaction conditions and product yields are shown in Table 1. In the



a) $n = 3$, $X = Cl$

b) $n = 2$, $X = Cl$

c) $n = 2$, $X = F$

cases of Ia and Ib, 79.3 and 100 % of indene was consumed and 85.2 and 87.8 % of the cycloadducts were obtained, respectively. Small amounts of indene dimer were also formed as a byproduct. However, with Ic, the cycloadduct (IIc) was yielded only 24.9 % and large amounts of the indene dimer was generated. When the ratio of indene to Ic was reduced (run 4), conversion and the yield of IIc were increased. As compared with Ia and Ib, Ic gave the cycloadduct in low yield. The result would be explained by the stability of the biradicals. The photo-sensitized cycloaddition is considered to proceed via biradical intermediates and a chlorine atom (in Ia, Ib) stabilizes the

TABLE 1

Photo-sensitized addition reaction of indene to cyclic fluoro-olefins

Run	Fluoro-olefin		Indene (mol)	Aceto-phenone (mol)	Irrad. time (hrs)	Conv. (%)	Yield (%)	
	(mol)	(mol)					cyclo-adduct	indene dimer
1	Ia	1.00	0.10	0.02	66	79.3	85.2	1.8
2	Ib	1.00	0.10	0.02	66	100	87.8	6.0
3	Ic	1.00	0.10	0.02	66	81.0	24.9	65.7
4	Ic	1.00	0.05	0.01	66	100	40.3	51.7
5*	Ia	1.00	0.10	0.02	20	100	88.9	10.3
6**	Ia	1.00	0.20	0.02	20	74.4	85.7	10.2

*) The reaction carried out using immersion well type photo-reactor.

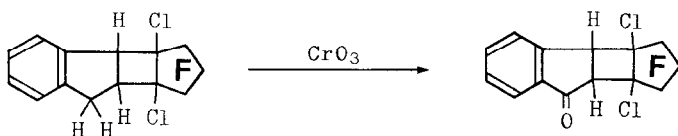
**) The reaction carried out adding indene dropwise in immersion well type photo-reactor.

adjoining carbon radical much more than a fluorine atom (in Ic) does. When an immersion well type photo-reactor was used (run 5), the conversion and the yield are high even under shorter irradiation time. The best procedure established here for the preparative purpose (run 6) was the irradiation of a solution containing acetophenone, indene and excess fluoro-olefin in a Pyrex immersion well type photo-reactor. Indene should be added drop by drop during the irradiation.

Irradiations without acetophenone in a quartz ampoule gave small amounts of tarry product only, no cycloadducts were obtained.

The structures of cycloadducts were elucidated by means of their IR, NMR and mass spectra. In the mass spectra, the strongest peak of the cycloadducts corresponds to indene (m/e : 116, C_9H_8) which is generated by the cleavage of four membered ring.

Two stereoisomers, IIa and II'a , were obtained from Ia in the ratio 97 : 3. The predominant isomer (IIa) was estimated to have *exo* configuration on the basis of their NMR spectra. The NMR spectral data of IIa and II'a are shown in Table 2 together with those of IIIa and III'a , which were obtained from oxidation of IIa and II'a by chromium trioxide, respectively.



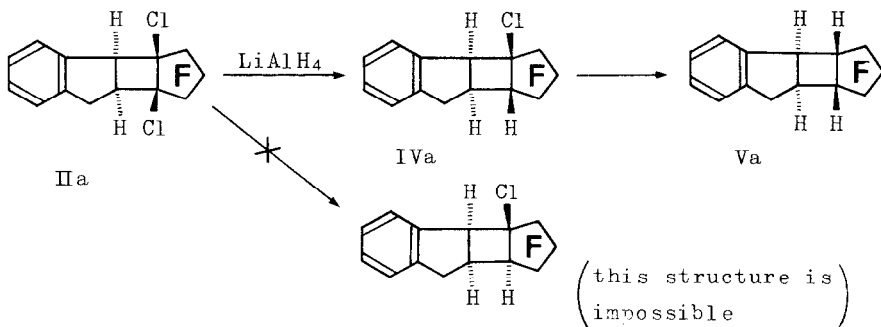
IIa : *exo*-isomer

IIIa : *exo*-isomer

II'a : *endo*-isomer

III'a : *endo*-isomer

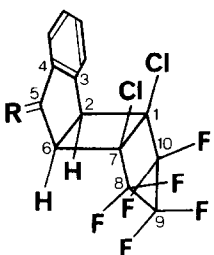
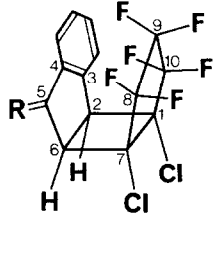




The configuration of IIa was further characterized by the replacement of chlorines by hydrogens and measurement of vicinal coupling constants between hydrogens on four membered ring. Reduction of IIa by lithium aluminum hydride afforded Va in 78.7 % yield, together with IVa in 18.4 % yield. Monitoring

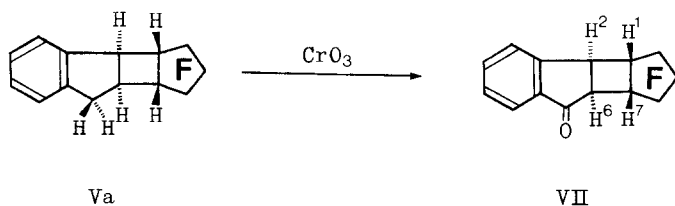


by g.l.c. showed that the reduction proceeded stepwise. The reduction seems to proceed with retention of configuration, because one of the chlorines of IIa can not be substituted with inversion. The proton NMR spectrum of Va could not be analyzed owing to complex signal overlapping. Oxidation of Va by chromium trioxide was tried and VII was obtained in 55.8 % yield. Removal of the hydrogens on 5 position of Va made the NMR spectrum of VII more simple. The signals of hydrogens

TABLE 2

The NMR spectral data of the cycloadducts from Ia and their oxidation products.

Compound				
	IIa	IIIa	II'a	III'a
R	H ₂	O	H ₂	O
Chemical shifts (ppm)				
C ₆ H ₄	7.1 ~ 7.3 m	7.4 ~ 7.9 m	7.0 ~ 7.5 m	7.4 ~ 7.9 m
	3.30) 3.56)	— —	3.22) 3.59)	— —
C ² -H	4.28 d	4.25 d	4.60 d	4.61 d
C ⁶ -H	3.63 d-d	3.64 d-d	3.92 t	3.88 d-d
	32.3) 52.1)	33.9) 53.3)	21.8) 48.5)	25.1) 46.1)
	43.5) 58.8)	43.8) 59.2)	49.2) 57.3)	46.1) 56.7)
	30.5) 54.7)	30.5) 53.3)	19.8) 48.4)	22.1) 48.6)
Coupling constants (Hz)				
H-C ⁵ -H	17.7	—	18.7	—
H-C ⁵ -C ⁶ -H	9.5	—	11.5	—
H-C ² -C ⁶ -H	6.6	6.0	11.3	9.3
F-C ⁸ -F	241	243	252	253
F-C ⁹ -F	260	254	253	255
F-C ¹⁰ -F	247	243	257	254



on 2 and 6 position appeared in two doublet pairs : $\delta(\text{H}^2)$ 4.01, $\delta(\text{H}^6)$ 3.32, $J(\text{H}^2-\text{H}^6) = 5$ Hz. The line breadths of the signals showed that values of $J(\text{H}^1-\text{H}^2)$ and $J(\text{H}^6-\text{H}^7)$ were less than 2 Hz. Although the vicinal coupling constants between hydrogens on four membered rings are sensitive to many factors, such as ring strain and substituents, the predominant factor is dihedral angles. The vicinal coupling constants between cis protons usually exceed those between trans protons [8]. The small $J(\text{H}^1-\text{H}^2)$ and $J(\text{H}^6-\text{H}^7)$ values indicate that these hydrogens are on the opposite side of the plane of four membered ring to one another. Therefore, VII has the *exo* configuration.

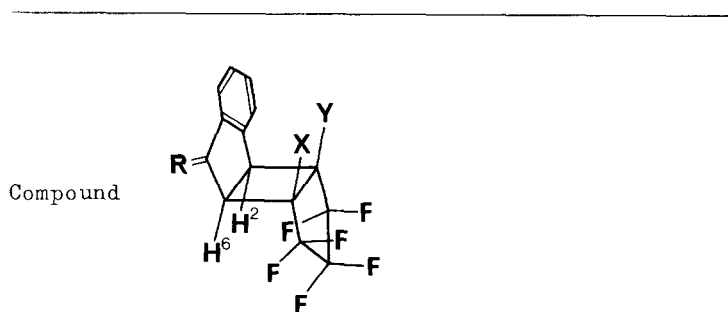
The study on structure of IIa by X-ray crystallography is now under way.

Two kinds of structure, A and B, are possible for IVa.



The structure was determined by the chemical shifts of H^2 and H^6 (Table 3). On the four membered ring, it is found that the resonance of hydrogen is shifted down-field by vicinal chlorine. As also shown in Table 3, the same shifts are observed more clearly in the case of IIIa, VI and VII, the oxidation products of IIa, IVa and Va. Since only one kind of product was obtained as IVa, the chlorine on 7 position was thought to be selectively reduced at first by lithium aluminum hydride.

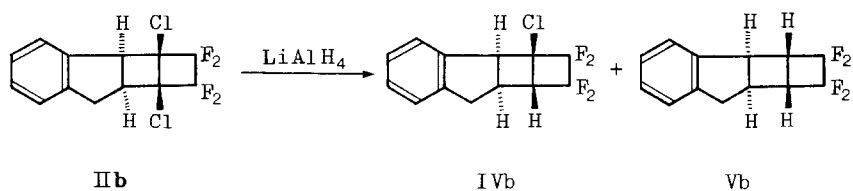
TABLE 5

Chemical shifts of H² and H⁶ (ppm)

	R	X	Y	H ⁶	H ²
IIa	H ₂	Cl	Cl	3.63	4.28
IVa	H ₂	H	Cl	3.1 ~ 3.4*	4.23
Va	H ₂	H	H	3.1 ~ 3.4*	3.83
IIIa	O	Cl	Cl	3.64	4.25
VI	O	H	Cl	3.23	4.37
VII	O	H	H	3.32	4.01

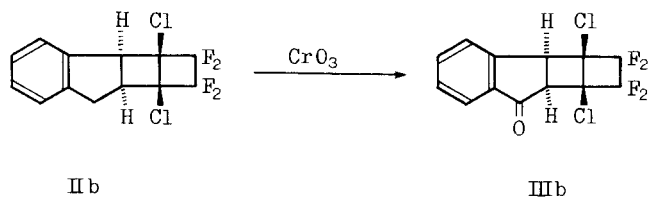
*) overlapped with peaks of other hydrogens

In the photo-cycloaddition of the other cyclic fluoro-olefins (Ib and Ic), only *exo*-isomers (IIb and IIc) were obtained and their *endo*-isomers were not detected. The configuration of IIb is estimated in the same manner as the case of IIa described above. Reduction of IIb by lithium aluminum hydride gave IVb and Vb in 42.5 % and 56.7 % yield, respectively. The vicinal H-H coupling constants of IVb and

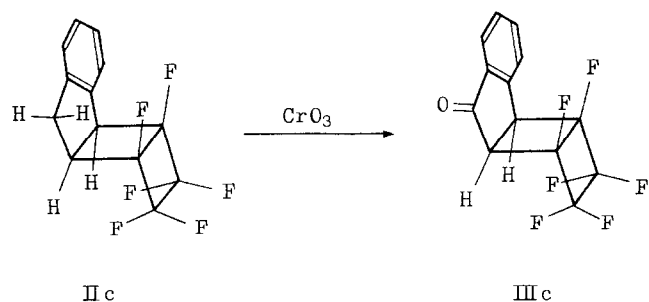


Vb indicated the *exo* configuration.

The oxidation of IIb afforded IIIb in 90.5 % yield.



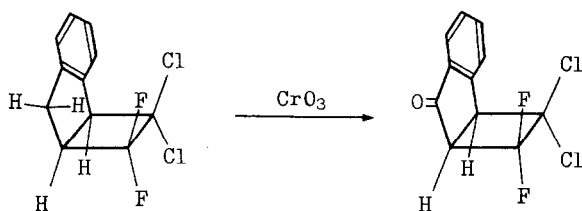
The NMR spectrum of IIc is too complicated, so the configuration is estimated by NMR of IIIc, the oxidation product of IIc.



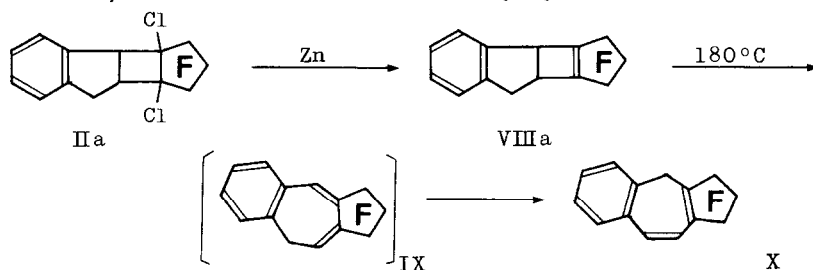
The coupling constants between hydrogens and fluorines on four membered ring of IIIc are as follows: $J(\text{H}^2-\text{F}^1) = 7.1 \text{ Hz}$, $J(\text{H}^6-\text{F}^7) = 5.9 \text{ Hz}$, $J(\text{H}^2-\text{F}^7) < 1 \text{ Hz}$, $J(\text{H}^6-\text{F}^1) = 2.0 \text{ Hz}$.

The relation between the vicinal H-F coupling constants and the conformations of cyclobutanes has been known. However, when the molecules are statically planar or in dynamic equilibrium between nonplanar conformations, the vicinal H-F coupling constants are thus averaged to become nearly equal,

having intermediate magnitude [9]. Therefore, in the case of IIIc, no configurational information was obtained from the vicinal H-F coupling constants. The small values of coupling constants between hydrogens and fluorines crossing the four membered ring seem to indicate that the hydrogens and fluorines are on the opposite side of the ring plane [10]. The resonance peak of F⁷ of IIIc shifted 10.2 ppm down-field from that of IIc. The shift is due to the electric field effect of the neighboring carbonyl group. A similar shift is observed in the oxidation product of the cycloadduct between indene and 1,1-dichloro-2,2-difluoroethylene [11].

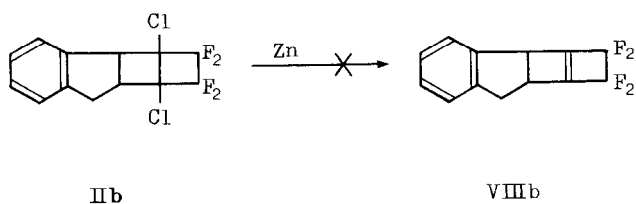


Dechlorination of IIa by zinc powder afforded VIIIa quantitatively. Upon heating of VIIIa at 180°C, it underwent a thermal ring expansion, followed by a 1,5-hydrogen migration to give X in 86.2 % yield. The NMR spectrum of the product shows the presence of isolate methylene protons (δ : 3.43, singlet) and adjacent two vinyl protons (δ : 6.48, doublet and δ : 7.38 doublet of triplet; J = 11.4 Hz). This is in good agreement with the structure X but not with the structure IX. A simple ring expansion product (IX) was not detected. The 1,5-hydrogen migration in tropyridenes has been known and explained by intramolecular mechanism [12].

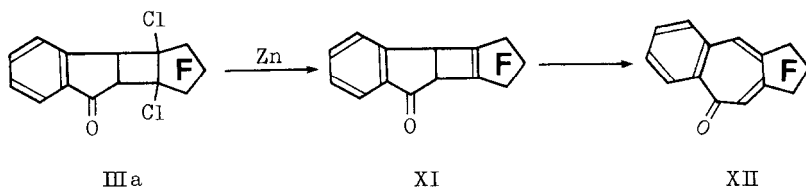


The mass spectra of VIIIa and X give an identical pattern of fragmentation. The isomerization of VIIIa to X seems to occur in a mass spectrometer before ionization.

An attempt of the similar dechlorination of IIb was unsuccessful even at 160°C, probably due to the highly strained structure of VIIIb.

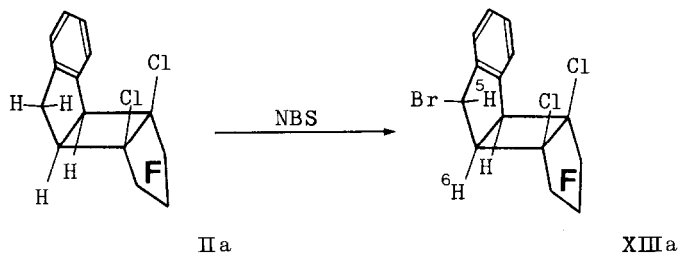


Dechlorination of IIIa afforded XI in 78.9 % yield. When XI was heated at 180°C, the product (XII) having the benzotroponone structure was obtained in 66.7 % yield.



The ring opening reaction of cyclobutene derivatives has been well known and the Woodward-Hoffmann's rule predicts that the thermal cleavage of cyclobutene occurs con-rotatory [13]. However, for a compound having a cyclobutene ring fused to a five membered ring such as bicyclo[3.2.0]heptene-6, the con-rotatory cleavage should be very difficult for steric reason. The ring expansion reaction of some derivatives of bicyclo[3.2.0]heptene-6 was reported to proceed dis-rotatory under more vigorous conditions, at a temperature higher than 400°C [5,14]. It is surprising that the ring expansion reaction of VIIIa and XI occurred at relatively lower temperature of 180°C in spite of forbiddenness by Woodward-Hoffmann's rule. This is probably due to their highly strained structures.

Bromination of IIa by N-bromosuccinimide gave the monobromide (XIIIa) in quantitative yield.



In the NMR spectrum of XIIIa , the signal of the hydrogen on 5 position appears as singlet at 5.83 ppm being shifted down-field by the geminal bromine. The singlet peak indicated that the magnitude of coupling constant between H^5 and H^6 is less than 1 Hz. In view of the relationship between vicinal H-H coupling constants and dihedral angles [15], H^5 is considered to be opposite side of the five membered ring plane from H^6 . Bromine substitution occurred on sterically favorable position of hydrogen of methylene group with high selectivity. Even excess N-bromosuccinimide did not result in further bromine substitution. The irradiation of IIa with bromine in tetrachloromethane afforded the same product (XIIIa) in 93.2 % yield

Similar brominations of IIb and IIc by N-bromosuccinimide gave the corresponding monobromides, XIIIb and XIIIc , in quantitative yield.

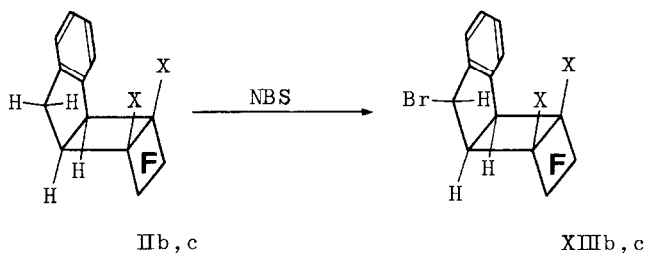
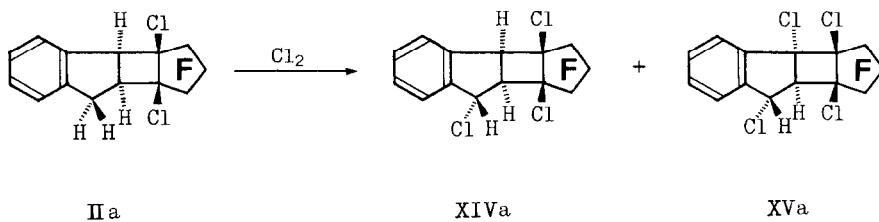
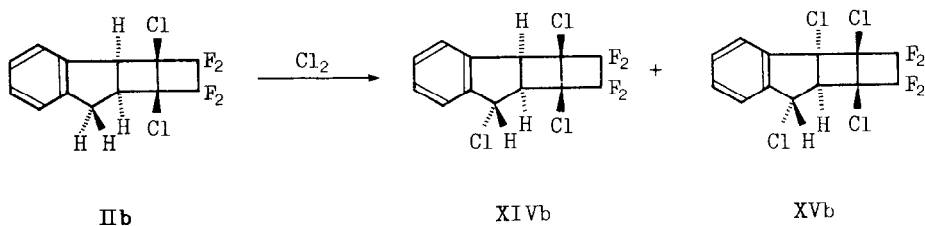


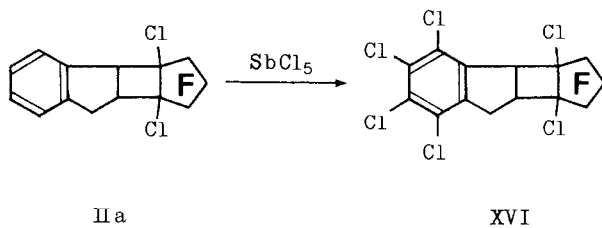
Photo-chlorination of IIa gave the monochloride (XIVa) in 75.8 % yield together with the small amounts (7.0 %) of dichloride (XVa). In analogy with the case of bromination the same position of the hydrogen was replaced by chlorine at



first selectively, but further chlorination occurred on a hydrogen of 2 position. A similar photo-chlorination of IIb afforded XIVb and XVb in 79.4 % and 8.3 % yield, respectively.



All the aromatic hydrogens of IIa were replaced by chlorine upon heating at 160°C with antimony pentachloride to give XVI in 80.2 % yield.



EXPERIMENTAL

Apparatus

The melting points were determined on Mettler FP1 with the elevating rate of 2°C/min. The IR and mass spectra were measured using a Hitachi Model EPI-2 grating spectrometer and

Model RMU-7 double-focusing mass spectrometer at 70 eV, respectively. The NMR spectra were obtained on Hitachi Model R-22 (90 MHz) using TMS as an internal standard for ^1H , and on Model R-20B (56.45 MHz) using trifluoroacetic acid as an external standard for ^{19}F . The analytical g.l.c. was carried out in a stainless steel column (3m long \times 3 mm diameter) packed with 20 % Silicone DC-QF1-Chromosorb W. In a preparative scale work an aluminum column (6m long \times 10 mm diameter ; 20 % Silicone DC-QF1-Chromosorb W) was used on a Varian Model 920.

Starting materials

Commercially available 1,2-dichlorohexafluorocyclopentene-1 (Ia), 1,2-dichlorotetrafluorocyclobutene-1 (Ib) and indene were used after distillation. Hexafluorocyclobutene-1 (Ic) was prepared from 1,2-dichlorohexafluorocyclobutane by dechlorination. All the other chemicals were of reagent grade and used as received.

Photo-cycloaddition reaction

endo- and *exo*-1,7-Dichloro-8,8,9,9,10,10-hexafluoro-3,4-benzotricyclo[5.3.0.0^{2,6}]decane (II'a and II a) : (a) An addition reaction in a Pyrex ampule

A mixture of indene (11.6 g, 0.10 mole), Ia (245 g, 1.00 mole) and acetophenone (2.4 g, 0.02 mole) sealed in a Pyrex ampule was irradiated by a 100W high pressure mercury lamp at room temperature for 66 hours. After recovery of excess Ia by distillation, the residue was allowed to stand overnight. Cycloadduct (II a) precipitated as colorless needles and was separated by filtration. The filtrate was further separated by vacuum distillation into indene (1.7 g, 14.8 % recovered), acetophenone (2.2 g), a mixture (9.7 g) of II a and II'a, and the indene dimer (0.2 g, 1.8 %, mp. 109.5°C, lit. 109.5~111°C [4]). The *endo*-isomer (II'a) was isolated by preparative g.l.c. as colorless needles (0.7 g, 2.3 %) : mp. 80~82°C ; mass *m/e*(relative abundance) 360 (0.4) M^+ , 325 (30.8),

289 (6.2), 219 (6.5), 116 (100), 115 (24.6) ; NMR (5 % CDCl_3 solution) δ 7.0~7.5 (m, 4H), 3.22 and 3.59 (AB, 2H, $J_{\text{gem}} = 18.7$ Hz), 3.92 (t-t, 1H, $J = 11.5$ Hz), 4.59 (d-d, 1H, $J = 11.3$ Hz), 19.8 and 48.4 (AB, 2F, $J_{\text{gem}} = 257$ Hz), 21.8 and 48.5 (AB, 2F, $J_{\text{gem}} = 253$ Hz), 49.2 and 57.3 (AB, 2F, $J_{\text{gem}} = 252$ Hz) ; elemental analysis Found C 46.56 %, H 2.41 % Calcd. for $\text{C}_{14}\text{H}_8\text{Cl}_2\text{F}_6$ C 46.57 %, H 2.23 %. The total yield of the *exo*-isomer (IIa) was 79.2 % (24.4 g). Recrystallization from ethanol gave colorless needles : mp. 77.1°C ; bp. 136°C/8 mmHg ; mass m/e (relative abundance) 360 (1.2) M^+ , 325 (24.9), 289 (3.8), 219 (3.8), 116 (100), 115 (22.5) ; NMR (20 % CDCl_3 solution) δ 7.1~7.3 (m, 4H), 3.30 and 3.56 (AB, 2H, $J_{\text{gem}} = 17.7$ Hz), 3.63 (d-d, 1H, $J = 9.5$ and 6.6 Hz), 4.28 (d, 1H), 30.3 and 54.7 (AB, 2F, $J_{\text{gem}} = 247$ Hz), 43.5 and 58.8 (AB, 2F, $J_{\text{gem}} = 260$ Hz), 32.3 and 52.1 (AB, 2F, $J_{\text{gem}} = 241$ Hz) ; elemental analysis Found C 46.69 %, H 2.35 % Calcd. for $\text{C}_{14}\text{H}_8\text{Cl}_2\text{F}_6$ C 46.57 %, H 2.23 %.

(b) An addition reaction in an immersion well type reactor

A mixture of indene (11.6 g, 0.10 mole), Ia (245 g, 1.00 mole) and acetophenone (2.4 g, 0.02 mole) was irradiated for 20 hours in an immersion well type Pyrex photo-reactor (300 ml capacity, with a water-cooled 100 W mercury lamp) under an argon atmosphere. IIa (32.1 g, 88.9 %) containing about 3 % of II'a and the indene dimer (1.2 g, 10.3 %) were obtained.

exo-1,7-Dichloro-8,8,9,9-tetrafluoro-3,4-benzotricyclo-[5.2.0.0^{2,6}]nonane (IIb) : An addition reaction in a Pyrex ampule

The irradiation of a mixture of indene (11.6 g, 0.10 mole), Ib (195 g, 1.00 mole) and acetophenone (2.4 g, 0.02 mole) gave IIb (27.3 g, 87.8 %) and indene dimer (0.7 g, 6.0 %). Recrystallization of IIb from ethanol gave colorless plates : mp. 81.8°C ; mass m/e (relative abundance) 310 (3.5) M^+ , 275 (13.9), 239 (8.2), 219 (6.5), 177 (11.3), 116 (100), 115 (14.6) ; NMR (20 % CDCl_3 solution) δ 7.1~7.4 (m, 4H), 3.40 (d, 1H, $J = 7.2$ Hz), 3.44 (d, 1H, $J = 2.4$ Hz), 3.68 (d-d-d, 1H), 4.31 (d, 1H, $J = 5.4$ Hz), 37.2 and 39.0

(AB, 2F, $J_{gem} = 203$ Hz), 38.6 and 39.4 (AB, 2F, $J_{gem} = 198$ Hz) ; elemental analysis Found C 49.86 %, H 2.80 % Calcd. for $C_{13}H_8Cl_2F_4$ C 50.19 %, H 2.59 %.

exo-1,7,8,8,9,9-Hexafluoro-3,4-benzotricyclo[5.2.0.0^{2,6}]-nonane (IIc) : An addition reaction in a Pyrex ampule

The irradiation of a mixture of indene (11.6 g, 0.10 mole) , Ic (162 g, 1.00 mole) and acetophenone (2.4 g, 0.02 mole) gave unchanged indene (2.2 g, 19.0 % recovered), IIc (5.6 g, 24.9 %) and indene dimer (6.6 g, 65.7 %).

Another run was carried out in a different molar ratio. The irradiation of a mixture of indene (5.8 g, 0.05 mole), Ic (162 g, 1.00 mole) and acetophenone (1.2 g, 0.01 mole) gave IIc (5.6 g, 40.3 %) and indene dimer (3.0 g, 51.7 %). Recrystallization from ethanol of IIc gave colorless plates : mp. 53.8°C ; bp. 121°C/11 mmHg ; mass *m/e* (relative abundance) 278 (14.5) M^+ , 177 (12.5), 132 (4.7), 116 (100), 115 (14.3) ; NMR (20 % $CDCl_3$ solution) δ 7.1~7.3 (m, 4H), 3.30~3.45 (m, 3H), 4.20 (m, 1H), 44.0 and 53.9 (AB, 2F, $J_{gem} = 219$ Hz), 44.1 and 55.3 (AB, 2F, $J_{gem} = 219$ Hz), 99.8 (d-m, 1F, $J = 26.0$ Hz), 111.9 (d-m, 1F) ; elemental analysis Found C 55.92 %, H 2.85 % Calcd. for $C_{13}H_8F_6$ C 56.13 %, H 2.90 %.

Reduction

exo-1-Chloro-8,8,9,9,10,10-hexafluoro-3,4-benzotricyclo-[5.3.0.0^{2,6}]decane (IVa) and *exo*-8,8,9,9,10,10-Hexafluoro-3,4-benzotricyclo[5.3.0.0^{2,6}]decane (Va)

Lithium aluminum hydride (1.5 g, 0.04 mole) and 20 ml of anhydrous ether were placed in a 100 ml Erlenmeyer flask ; a solution of IIa (3.6 g, 0.01 mole) in 20 ml of ether was then added. With stirring, the mixture was refluxed for 10 hours and allowed to stand overnight at room temperature. The mixture was poured into dilute sulfuric acid and the ether layer was separated and dried by magnesium sulfate. After removal of the solvent, a mixture was separated by preparative g.l.c. into IVa (0.6 g, 18.4 %) as colorless prisms (recryst-

tallized from ethanol) : mp. 64.4°C ; mass m/e (relative abundance) 326 (0.3) M^+ , 291 (1.2), 271 (0.9), 201 (1.5), 116 (100), 115 (20.7) ; NMR (20 % CCl_4 solution) δ 7.0~7.3 (m, 4H), 2.5~3.6 (complex m, 4H), 4.23 (broad d, 1H, $J = 6.5$ Hz), 31.7 and 48.7 (AB, 2F, $J = 257$ Hz), 33.7 and 51.3 (AB, 2F, $J = 253$ Hz), 46.6 and 63.1 (AB, 2F, $J = 260$ Hz) ; elemental analysis Found C 51.42 %, H 2.77 % Calcd. for $C_{14}H_9ClF_6$ C 51.48 %, H 2.78 % and Va (2.3 g, 78.7 %) as colorless oil : bp. 97~98°C/ 4mmHg ; n_D^{20} 1.4692 ; mass m/e (relative abundance) 292 (4.4) M^+ , 291 (2.9), 191 (2.1), 177 (1.9), 140 (7.7), 116 (100), 115 (23.1) ; NMR δ 7.13 (broad s, 4H), 2.5~3.5 (complex m, 5H), 3.83 (broad d, 1H, $J = 5$ Hz), 30.7 and 51.3 (AB, 2F, $J = 248$ Hz), 33.1 and 48.7 (AB, 2F, $J = 255$ Hz), 46.2 and 57.4 (AB, 2F, $J = 257$ Hz) ; elemental analysis Found C 57.45 %, H 3.39 % Calcd. for $C_{14}H_{10}F_6$ C 57.54 %, H 3.45 %.

exo-1-Chloro-8,8,9,9-tetrafluoro-3,4-benzotricyclo[5.2.0.0^{2,6}]nonane (IVb) and *exo*-8,8,9,9-Tetrafluoro-3,4-benzotricyclo[5.2.0.0^{2,6}]nonane (Vb)

In a similar procedure, the reaction of IIb (1.6 g, 0.005 mole) and lithium aluminum hydride (0.8 g, 0.021 mole) gave IVb (0.6 g, 42.5 %) as colorless needles (recrystallized from chloroform) : mp. 129.2°C ; mass m/e (relative abundance) 276 (1.1) M^+ , 241 (2.6), 201 (2.9), 177 (2.6), 170 (2.3), 164 (2.6), 141 (2.3), 116 (100), 115 (15.8) ; NMR (20 % $CDCl_3$ solution) δ 7.1~7.4 (m, 4H), 2.7~3.6 (complex m, 4H), 4.22 (broad d, 1H, $J = 5$ Hz), 36.6 and 39.3 (overlapped two AB pairs, 4F, $J = 209$ Hz) ; elemental analysis Found C 56.53 %, H 2.97 % Calcd. for $C_{13}H_9ClF_4$ C 56.44 %, H 3.28 % and Vb (0.8 g, 56.7 %) as colorless oil : n_D^{20} 1.4950 ; mass m/e (relative abundance) 242 (9.4) M^+ , 201 (3.0), 177 (5.4), 165 (5.2), 141 (10.8), 116 (100), 115 (21.2) ; NMR (20 % $CDCl_3$ solution) δ 7.0~7.3 (m, 4H), 2.4~3.5 (complex m, 5H), 3.92 (broad d, 1H, $J = 5$ Hz), 37.0 (m, 2F), 36.4 and 41.1 (AB, 2F, $J = 209$ Hz) ; elemental analysis Found C 63.97 %, H 4.00 % Calcd. for $C_{13}H_{10}F_4$ C 64.46 %, H 4.16 %.

Oxidation*exo*-1,7-Dichloro-8,8,9,9,10,10-hexafluoro-3,4-benzotricyclo-[5.3.0.0^{2,6}]deca-5-one (IIIa)

To a solution of chromium trioxide (8.0 g, 0.080 mole) in 30 ml of water, a solution of IIa (7.2 g, 0.020 mole) in 50 ml of glacial acetic acid was added ; the mixture was then refluxed for 7 hours and poured into an ice-cooled aqueous sodium hydrogensulfite solution. Ether (300 ml) was then added and the organic layer separated was washed by 50 ml of water and dried over magnesium sulfate. The solvent was allowed to evaporate to give a white solid (8.4 g). Recrystallization from ethanol gave IIIa (6.4 g, 85.3 %) as colorless prisms : mp. 113.4°C ; IR $\nu_{C=O}$ 1727 cm^{-1} ; mass m/e (relative abundance) 374 (9.7) M^+ , 339 (100), 319 (9.2), 206 (7.6), 175 (7.3), 130 (97.6), 102 (26.2) ; NMR (5 % CCl_4 solution) δ 7.4~7.9 (m, 4H), 3.64 (d-d, 1H, $J = 6$ Hz and 3 Hz), 4.25 (d, 1H, $J = 6$ Hz), 30.5 and 53.3 (AB, 2F, $J = 243$ Hz) 33.9 and 53.3 (AB, 2F, $J = 243$ Hz), 43.8 and 59.2 (AB, 2F, $J = 254$ Hz) ; elemental analysis Found C 44.57 %, H 1.63 % Calcd. for $C_{14}H_6OCl_2F_6$ C 44.83 %, H 1.62 %.

endo-1,7-Dichloro-8,8,9,9,10,10-hexafluoro-3,4-benzotri-cyclo[5.3.0.0^{2,6}]deca-5-one (IIIa')

By a similar procedure, oxidation of about equal amounts of mixture (1.8 g, 0.005 mole) of IIa and II'a by chromium trioxide gave the mixture (1.5 g) of IIIa and IIIa' as white solid. Fractional crystallization from ethanol gave IIIa' (0.3 g) as colorless prisms : mp. 145.1°C ; IR $\nu_{C=O}$ 1724 cm^{-1} ; mass m/e (relative abundance) 374 (4.3) M^+ , 339 (100), 319 (16.5), 206 (13.7), 175 (10.8), 130 (64.7), 102 (20.1) ; NMR (20 % $CDCl_3$ solution) δ 7.4~7.9 (m, 4H), 3.88 (d-d, 1H, $J = 9$ Hz and 2 Hz), 4.61 (d, 1H, $J = 9$ Hz), 22.1 and 48.6 (AB, 2F, $J = 254$ Hz), 25.1 and 46.1 (AB, 2F, $J = 254$ Hz), 46.1 and 56.7 (AB, 2F, $J = 255$ Hz) ; elemental analysis Found C 44.85 %, H 1.58 % Calcd. for $C_{14}H_6OCl_2F_6$ C 44.83 %, H 1.62 %.

exo-1,7-Dichloro-8,8,9,9-tetrafluoro-3,4-benzotricyclo-
[5.2.0.0^{2,6}]nona-5-one (IIIb)

By a similar procedure, oxidation of IIb (1.6 g, 0.005 mole) by chromium trioxide gave IIIb (1.7 g, 90.5 %) as colorless needles (recrystallized from chloroform) : mp. 159.8°C ; IR $\nu_{C=O}$ 1724 cm^{-1} ; mass m/e (relative abundance) 324 (3.4) M^+ , 289 (100), 269 (15.8), 226 (8.5), 206 (14.6), 130 (12.1), 102 (9.0) ; NMR (5 % CDCl_3 solution) δ 7.4~8.0 (m, 4H), 3.83 (d, 1H, $J = 5$ Hz), 4.37 (d, 1H, $J = 5$ Hz), 37.8 (d, 2F, $J = 2$ Hz), 37.0 and 40.1 (AB, 2F, $J = 203$ Hz) ; elemental analysis Found C 47.70 %, H 1.97 % Calcd. for $\text{C}_{13}\text{H}_6\text{OCl}_2\text{F}_4$ C 48.03 %, H 1.86 %.

exo-1,7,8,8,9,9-Hexafluoro-3,4-benzotricyclo[5.2.0.0^{2,6}]nona-
5-one (IIIc)

By a similar procedure, oxidation of IIc (1.4 g, 0.005 mole) gave IIIc (1.3 g, 89.0 %) as colorless needles (recrystallized from ethanol) : mp. 121.6°C ; IR $\nu_{C=O}$ 1726 cm^{-1} ; mass m/e (relative abundance) 292 (100) M^+ , 272 (12.8), 253 (14.4), 245 (17.4), 223 (27.4), 195 (46.2), 164 (34.1), 130 (23.6), 104 (24.5) ; NMR (30 % CDCl_3 solution) δ 7.4~8.0 (m, 4H), 3.72 (d-d-d, 1H, $J = 6$ Hz, 4 Hz and 2 Hz), 4.34 (d-d, 1H, $J = 7$ Hz and 4 Hz), 97.9 (d-d-t, 1F, $J = 26$ Hz and 6 Hz), 101.1 (d-d-m, 1F, $J = 26$ Hz and 7 Hz), 41.3 and 53.9 (AB, 2F, $J = 214$ Hz), 42.4 and 53.1 (AB, 2F, $J = 218$ Hz) ; elemental analysis Found C 53.13 %, H 1.84 % Calcd. for $\text{C}_{13}\text{H}_6\text{OF}_6$ C 53.44 %, H 2.07 %.

exo-1-Chloro-8,8,9,9,10,10-hexafluoro-3,4-benzotricyclo-
[5.3.0.0^{2,6}]deca-5-one (VI)

By a similar procedure, oxidation of IVa (0.33 g, 0.001 mole) by chromium trioxide gave VI (0.26 g, 75.6 %) as colorless prisms : mp. 129.2°C ; IR $\nu_{C=O}$ 1718 cm^{-1} ; mass m/e (relative abundance) 340 (8.5) M^+ , 305 (24.4), 289 (3.1), 285 (2.1), 257 (3.0), 237 (2.2), 130 (100), 102 (24.6) ; NMR (10 % CDCl_3 solution) δ 7.4~8.0 (m, 4H), 3.06 (m, 1H), 3.23 (d, 1H, $J = 6.5$ Hz), 4.37 (d, 1H, $J = 6.5$ Hz), 31.1 and 54.5 (AB, 2F, $J = 248$ Hz), 32.7 and 48.8 (AB, 2F, $J = 256$ Hz), 45.4 and 59.6 (AB, 2F, $J = 261$ Hz) ;

elemental analysis Found C 49.09 %, H 2.04 % Calcd. for $C_{14}H_7OC1F_6$ C 49.36 %, H 2.07 %.

exo-8,8,9,9,10,10-Hexafluoro-3,4-benzotricyclo[5.3.0.0^{2,6}]-deca-5-one (VII)

By a similar procedure, oxidation of Va (1.2 g, 0.004 mole) gave VII (0.7 g, 55.8 %) as colorless prisms (recrystallized from ethanol) : mp. 103°C ; IR $\nu_{C=O}$ 1711 cm^{-1} ; mass m/e (relative abundance) 306 (18.3) M^+ , 278 (2.4), 177 (14.0), 130 (100), 102 (21.3) ; NMR (10 % $CDCl_3$ solution) δ 7.4~7.9 (m, 4H), 2.98 (m, 2H), 3.32 (d, 1H, $J = 5$ Hz), 4.01 (d, 1H, $J = 5$ Hz), 32.7 and 49.5 (AB, 2F, $J = 254$ Hz) 32.7 and 50.1 (AB, 2F, $J = 254$ Hz), 46.3 and 63.6 (AB, 2F, $J = 265$ Hz) ; elemental analysis Found C 55.12 %, H 2.41 % Calcd. for $C_{14}H_8OF_6$ C 54.92 %, H 2.63 %.

Dechlorination

8,8,9,9,10,10-Hexafluoro-3,4-benzotricyclo[5.3.0.0^{2,6}]deca-1(7)-ene (VIIIa)

To a solution of IIa (3.6 g, 0.01 mole) in 60 ml of ethanol, zinc powder (6.6 g) was added. Then with stirring, the mixture was refluxed for 4 hours and poured into dilute hydrochloric acid. The product was extracted with ether. Removal of the solvent yielded crystals, which were recrystallized from ethanol to give VIIIa (2.9 g, 100 %) as colorless prisms : mp. 149.6°C ; IR $\nu_{C=C}$ 1672 cm^{-1} ; mass m/e (relative abundance) 290 (100) M^+ , 289 (33.9), 239 (13.6), 221 (14.1), 219 (18.0), 201 (20.6), 190 (20.6), 170 (15.0) ; NMR (10 % $CDCl_3$ solution) δ 7.1~7.4 (m, 4H), 3.08 and 3.27 (AB, 2H, $J = 21$ Hz), 4.20 (m, 1H), 4.88 (d-m, 1H, $J = 4$ Hz), 32.0 (broad s, 2F), 31.8 and 33.8 (AB, 2F, $J = 248$ Hz), 46.2 (t-t, 2F, $J = 2.3$ Hz) ; elemental analysis Found C 57.91 %, H 2.86 % Calcd. for $C_{14}H_8F_6$ C 57.94 %, H 2.78 %.

8,8,9,9,10,10-Hexafluoro-3,4-benzotricyclo[5.3.0.0^{2,6}]deca-1(7)-ene-5-one (XI)

By a similar procedure, dechlorination of IIIa (1.9 g, 0.005 mole) by zinc powder (3.3 g) gave XI (1.2 g, 78.9 %)

as colorless prisms : mp. 119°C ; IR $\nu_{C=O}$ 1724 cm^{-1} , $\nu_{C=C}$ 1673 cm^{-1} ; mass m/e (relative abundance) 304 (14.4) M^+ , 276 (100), 226 (35.6), 207 (40.4), 176 (18.5), 157 (20.3) ; NMR (10 % CDCl_3 solution) δ 7.3~7.9 (m, 4H), 4.44 (d-t, 1H, $J = 4$ Hz and 7 Hz), 4.99 (q, 1H, $J = 4$ Hz), 32.8 (m, 2F), 32.3 and 34.8 (AB, 2F, $J = 248$ Hz), 46.1 (quintet, 2F, $J = 2.3$ Hz) ; elemental analysis Found C 55.09 %, H 2.07 % Calcd. for $\text{C}_{14}\text{H}_6\text{OF}_6$ C 55.28 %, H 1.99 %.

Thermal ring expansion

8,8,9,9,10,10-Hexafluoro-3,4-benzobicyclo[5.3.0]deca-1(7),5-diene (X)

A solution of VIIIa (2.9 g, 0.01 mole) in 30 ml of *o*-dichlorobenzene was refluxed for 2 hours. After the solvent was removed by vacuum distillation, solid residue was obtained and recrystallized from ethanol to give X (2.5 g, 86.2 %) as colorless prisms : mp. 44.5°C ; IR $\nu_{C=C}$ 1607 cm^{-1} and 1665 cm^{-1} ; mass m/e (relative abundance) 290 (100) M^+ , 289 (26.3), 271 (10.4), 240 (15.5), 219 (16.5), 201 (17.1), 190 (37.5), 170 (16.9) ; NMR (10 % CDCl_3 solution) δ 7.1~7.4 (m, 4H), 3.43 (broad s, 2H), 6.48 and 7.38 (AB, 2H, $J = 11.4$ Hz), 31.6 (broad s, 2F), 32.1 (d-t, 2F, $J = 4$ Hz) 50.3 (quintet, 2F, $J = 4$ Hz) ; elemental analysis Found C 57.60 %, H 2.82 % Calcd. for $\text{C}_{14}\text{H}_8\text{F}_6$ C 57.94 %, H 2.78 %.

8,8,9,9,10,10-Hexafluoro-3,4-benzobicyclo[5.3.0]deca-1,6-diene-5-one (XII)

By a similar procedure, pyrolysis of XI (0.6 g, 0.002 mole) gave XII (0.4 g, 66.7 %) as pale yellow plates : mp. 143.4°C ; IR $\nu_{C=O}$ 1596 cm^{-1} , $\nu_{C=C}$ 1618 cm^{-1} and 1670 cm^{-1} ; mass m/e (relative abundance) 304 (17.0) M^+ , 276 (100), 226 (33.3), 207 (36.1), 176 (14.9), 157 (18.1) ; NMR (5 % CDCl_3 solution) δ 7.8~7.9 (m, 4H), 7.31 (broad s, 1H), 8.53 (m, 1H), 32.8 (broad s, 2F), 35.6 (broad s, 2F), 57.7 (quintet, 2F, $J = 7$ Hz) ; elemental analysis Found C 55.32 %, H 1.94 % Calcd. for $\text{C}_{14}\text{H}_6\text{OF}_6$ C 55.28 %, H 1.99 %.

Brominationexo-5-Bromo-1,7-dichloro-8,8,9,9,10,10-hexafluoro-3,4-benzotricyclo[5.3.0.0^{2,6}]decane (XIIIa)

(a) Bromination by N-bromosuccinimide : A solution of IIa (3.6 g, 0.01 mole), N-bromosuccinimide (1.4 g, 0.008 mole) and benzoyl peroxide (0.001 g) in 50 ml of tetrachloromethane was refluxed for 1.5 hours under a nitrogen atmosphere. Precipitated succinimide was filtered off and the solvent was removed by distillation. The residue was separated by elution chromatography (on silica gel, using tetrachloromethane as an eluant) into IIa and XIIIa (3.5 g, quantitative yield) as a pale yellow oil : n_D^{20} 1.5170 ; mass m/e (relative abundance) 438 (0.05) M^+ , 359 (100), 324 (33.1), 289 (18.7), 277 (28.3), 219 (25.3), 188 (18.4), 115 (96.8) ; NMR (5 % CCl_4 solution) δ 7.0~7.6 (m, 4H), 3.90 (broad s, 1H, $J = 7$ Hz), 4.50 (d, 1H, $J = 7$ Hz), 5.83 (s, 1H), 29.1 and 54.1 (AB, 2F, $J = 247$ Hz), 33.4 and 51.6 (AB, 2F, $J = 245$ Hz), 43.5 and 58.6 (AB, 2F, $J = 263$ Hz) ; elemental analysis Found C 38.48 %, H 1.43 % Calcd. for $C_{14}H_7BrCl_2F_6$ C 38.22 %, H 1.60 %.

(b) Photo-bromination : A solution of IIa (3.6 g, 0.01 mole) and bromine (3.2 g, 0.02 mole) in 25 ml of tetrachloromethane was irradiated by a 100 W high pressure mercury lamp in a Pyrex flask for 16 hours. The reaction mixture was washed with a 10 % aqueous sodium hydrogensulfite and then a 10 % aqueous sodium hydrogencarbonate, and dried over magnesium sulfate. After removal of the solvent, the product was purified by elution chromatography to give XIIIa (4.1 g, 93.2 %).

exo-5-Bromo-1,7-dichloro-8,8,9,9-tetrafluoro-3,4-benzotricyclo[5.2.0.0^{2,6}]nonane (XIIIb)

By a procedure similar to that described in (a), the bromination of IIb (3.1 g, 0.01 mole) with N-bromosuccinimide (1.4 g, 0.008 mole) gave XIIIb (3.1 g, quantitative yield) as a colorless oil : n_D^{20} 1.5417 ; mass m/e (relative abundance) 388 (0.2) M^+ , 309 (88.0), 273 (39.1), 239 (32.5), 219

(22.0), 188 (18.8), 115 (100) ; NMR (20 % CCl₄ solution) δ 7.1~7.6 (m, 4H), 3.97 (d, 1H, $J = 5$ Hz), 4.48 (d, 1H, $J = 5$ Hz), 5.80 (s, 1H), 36.4 and 41.2 (AB, 2F, $J = 203$ Hz), 38.0 and 39.5 (AB, 2F, $J = 183$ Hz) ; elemental analysis Found C 40.46 %, H 1.90 % Calcd. for C₁₃H₇BrCl₂F₄ C 40.04 %, H 1.81 %.

exo-5-Bromo-1,7,8,8,9,9-hexafluoro-3,4-benzotricyclo-[5.2.0.0^{2,6}]nonane (XIIIc)

By a similar procedure, the bromination of IIc (1.8 g, 0.0065 mole) with N-bromosuccinimide (1.1 g, 0.0062 mole) gave XIIIc (2.2 g, quantitative yield) as a colorless oil : n_D^{20} 1.5030 ; mass m/e (relative abundance) 356 (0.14) M⁺, 277 (100), 257 (14.5), 237 (7.9), 195 (10.6), 188 (16.6), 177 (41.4), 115 (58.6) ; NMR (20 % CCl₄ solution) δ 7.0~7.6 (m, 4H), 3.69 (q, 1H, $J = 5$ Hz), 4.40 (d-d, 1H, $J = 7$ Hz and 5 Hz), 5.68 (s, 1H), 43.1 and 55.9 (AB, 2F, $J = 218$ Hz), 44.5 and 53.2 (AB, 2F, $J = 223$ Hz), 98.9 (d-m, 1F, $J = 28$ Hz), 111.6 (d-m, 1F, $J = 28$ Hz) ; elemental analysis Found C 44.15 %, H 2.09 % Calcd. for C₁₃H₇BrF₆ C 43.73 %, H 1.98 %.

Chlorination

exo-1,5,7-Trichloro-8,8,9,9,10,10-hexafluoro-3,4-benzotricyclo[5.3.0.0^{2,6}]decane (XIVA) and *exo*-1,2,5,7-Tetrachloro-8,8,9,9,10,10-hexafluorotricyclo[5.3.0.0^{2,6}]decane (XVa)

Chlorine (0.8 g, 0.011 mole) was absorbed by bubbling through a solution of IIa (3.6 g, 0.010 mole) in 200 ml of tetrachloromethane. The solution was irradiated for 20 minutes by a 100 W high pressure mercury lamp in a Pyrex flask, washed with a 10 % aqueous sodium hydrogensulfite and dried over magnesium sulfate. After removal of the solvent, the residue was distilled in *vacuo* to give the mixture (3.4 g) of XIVA and XVa in a ratio of 9 : 1. They were separated by preparative g.l.c. into XIVA (3.0 g, 75.8 %) : mp. 80.9°C (recrystallized from ethanol) ; bp. 120~121°C/3 mmHg ; mass m/e (relative abundance) 394 (2.5) M⁺, 359 (49.6), 324 (11.0), 323 (11.2), 289 (7.2), 219 (12.2), 188 (7.6), 150

(97.0), 115 (100) ; NMR (20 % CCl_4 solution) δ 7.0 ~ 7.5 (m, 4H), 3.77 (broad d, 1H, $J = 7$ Hz), 4.45 (d, 1H, $J = 7$ Hz), 5.75 (s, 1H), 29.4 and 54.3 (AB, 2F, $J = 250$ Hz), 33.4 and 52.1 (AB, 2F, $J = 246$ Hz), 43.7 and 58.9 (AB, 2F, $J = 261$ Hz) ; elemental analysis Found C 42.49 %, H 1.86 % Calcd. for $\text{C}_{14}\text{H}_7\text{Cl}_3\text{F}_6$ C 42.51 %, H 1.78 % and XVa (0.3 g, 7.0 %).

exo-1,5,7-Trichloro-8,8,9,9-tetrafluoro-3,4-benzotricyclo-[5.2.0.0^{2,6}]nonane (XIVb) and *exo*-1,2,5,7-Tetrachloro-8,8,9,9-tetrafluoro-3,4-benzotricyclo[5.2.0.0^{2,6}]nonane (XVb)

By a similar procedure, chlorination of IIb (1.6g, 0.005 mole) gave XIVb (1.4 g, 79.4 %) as a colorless oil : n_D^{20} 1.5277 ; mass m/e (relative abundance) 344 (5.9) M^+ , 309 (29.4), 274 (21.0), 239 (13.4), 238 (10.9), 219 (14.3), 211 (16.0), 188 (15.1), 150 (100), 115 (80.7) ; NMR (20 % CDCl_3 solution) δ 7.2 ~ 7.4 (m, 4H), 3.86 (d, 1H, $J = 5$ Hz), 4.48 (d, 1H, $J = 5$ Hz), 5.72 (s, 1H), 36.5 and 40.8 (AB, 2F, $J = 203$ Hz), 37.7 and 39.5 (AB, 2F, $J = 172$ Hz) ; elemental analysis Found C 45.16 %, H 2.13 % Calcd. for $\text{C}_{13}\text{H}_7\text{Cl}_3\text{F}_4$ C 45.19 %, H 2.04 % and XVb as a colorless oil : n_D^{20} 1.5343 ; mass m/e (relative abundance) 378 (0.1) M^+ , 343 (32.4), 307 (18.7), 273 (18.7), 238 (18.7), 237 (17.3), 184 (100), 149 (71.9) ; elemental analysis Found C 41.37 %, H 1.70 % Calcd. for $\text{C}_{13}\text{H}_6\text{Cl}_4\text{F}_4$ C 41.09 %, H 1.59 %.

exo-1,7-Dichloro-8,8,9,9,10,10-hexafluoro-3,4-(tetrachlorobenzo)tricyclo[5.3.0.0^{2,6}]decane (XVI)

The mixture of IIa (2.0 g, 0.0055 mole) and antimony pentachloride (6.0 g, 0.020 mole) was heated at 160°C for 3 hours and poured into ice cooled water. The product was extracted by 50 ml of dichloromethane and the extract was dried over magnesium sulfate. The solvent was allowed to evaporate to give a pale yellow solid (3.0 g). Recrystallization from hexane gave XVI (2.2 g, 80.2 %) as pale yellow plates : mp. 164.2°C ; mass m/e (relative abundance) 496 (4.5) M^+ , 461 (33.9), 426 (73.2), 391 (27.7), 321 (26.8), 252 (100) ; NMR (10 % CCl_4 solution) δ 3.36 and 3.74 (AB, 2H, $J = 19$ Hz), 3.64 (d-d, 1H, $J = 11$ Hz and 7 Hz), 4.51 (d, 1H, $J = 7$ Hz

), 31.3 and 54.3 (AB, 2F, $J = 244$ Hz), 31.9 and 53.2 (AB, 2F, $J = 241$ Hz), 44.3 and 59.2 (AB, 2F, $J = 263$ Hz); elemental analysis Found C 33.77 %, H 0.73 % Calcd. for $C_{14}H_4Cl_6F_6$ C 33.71 %, H 0.81 %.

All the fluorine-containing polycyclic compounds synthesized in this work are new compounds.

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