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Photo-cycloaddition of Indene to Chlorofluoroethylenes and Some Reactions Concerning the Adducts

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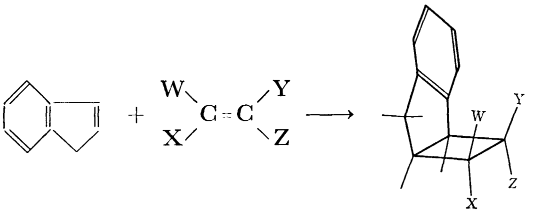
Benzophenone photo-sensitized addition of indene to chlorofluoroethylenes [trichlorofluoroethylene, 1,2-dichloro-1,2-difluoroethylene, 1,1-dichloro-2,2-difluoroethylene, chlorotrifluoroethylene, tetrafluoroethylene] afforded 6,6,7,7-tetrahalogeno-2,3-benzobicyclo[3.2.0]hept-2-enes as corresponding cycloadducts. The structure of the cycloadducts obtained from unsymmetrical chlorofluoroethylenes shows that the addition reaction proceeds with good regioselectivity. Some reactions such as oxidation, reduction, dechlorination, and halogenation of the cycloadducts were also examined.

Fluoro olefins are known to undergo cycloaddition reaction upon heating.[1] In fact, most fluorine-containing cyclobutane derivatives have been synthesized by the thermal cycloaddition of fluoro olefins and by subsequent reactions of these cycloadducts. In contrast, only a few investigations on photo-cycloaddition of fluoro olefins have been reported.[2–4] Since the photo-cycloaddition reaction would be expected to give different results from the thermal reaction, we investigated the photo-sensitized addition of indene to chlorofluoroethylenes [trichlorofluoroethylene (TCFE), 1,2-dichloro-1,2-difluoroethylene (*sym*-DCDFE), 1,1-dichloro-2,2-difluoroethylene (*unsym*-DCDFE), chlorotrifluoroethylene (CTFE), tetrafluoroethylene (TFE)] as a part of our studies on syntheses of fluorine-containing fused polycyclic compounds.[5] It is known that the cycloadditions of *unsym*-DCDFE, CTFE, and TFE take place thermally but those of indene, *sym*-DCDFE and TCFE do not.[1] The effect of fluorine recently has become of considerable interest in photochemistry[4,6] in light of the fact that 5-fluorouracil has been reported to have superior regioselectivity compared with unsubstituted uracil in the photo-cycloaddition reaction with several olefins. Accordingly, we have investigated the regioselectivity and stereoselectivity in the photo-cycloaddition of indene to chlorofluoroethylenes by elucidating the structure of the cycloadducts by means of NMR spectroscopy.

Results and Discussion

Irradiation (>300 nm) of indene and an excess of chlorofluoroethylenes in the presence of benzophenone



1a W=F; X,Y,Z=Cl
1b X=F; W,Y,Z=Cl
1c Y=F; W,X,Z=Cl
1d Z=F; W,X,Y=Cl
2a W,Y=F; X,Z=Cl
2b W,Z=F; X,Y=Cl
2c X,Y=F; W,Z=Cl
2d X,Z=F; W,Y=Cl
3a W,X=F; Y,Z=Cl
3b Y,Z=F; W,X=Cl
4a W,X,Y=F; Z=Cl
4b W,X,Z=F; Y=Cl
4c W,Y,Z=F; X=Cl
4d X,Y,Z=F; W=Cl
5 W,X,Y,Z=F

as a sensitizer gave 6,6,7,7-tetrahalogeno-2,3-benzobicyclo[3.2.0]hept-2-enes as the corresponding cycloadducts (**1**—**5**).

Four different reaction conditions were employed (Methods A—D). In Methods A and B, irradiations were carried out in a Pyrex ampoule, while in Methods C and D, an immersion well photo-reactor was used. In order to study the effect of dilution with solvent, no solvent was used in Method B. Since TFE has a very low boiling point and polymerizes explosively, in Method D, TFE was bubbled into a solution of indene and benzophenone in 1,1,2-trichloro-1,2,2-trifluoroethane followed by irradiation in an immersion well reactor. In this procedure, the concentration of absorbed TFE was not determined. The reaction conditions and product yields are shown in Table 1.

As compared with Method A, Method B gave slightly higher conversion and slightly lower yield of cycloadduct. Hence, there are no marked differences in results from Methods A and B. When an immersion well photo-reactor was used (Method C), the conversions and yields were high even with shorter irradiation times.

Using Method A, the reaction of *unsym*-DCDFE gave high conversion (98.3%), while reactions of other chlorofluoroethylenes showed somewhat lower conversions (63—70%). In all cases, the yields of the cycloadducts **1**—**4** were similar (55—65%). Using Methods C and D, most of the indene (94%) was consumed and cycloadducts were obtained in good yields (84—85%) from TCFE and *unsym*-DCDFE. With TFE, the yield of cycloadduct (**5**) was very low and large amounts of high-boiling products were obtained.

The yields of the cycloadducts obtained from chlorofluoroethylenes are as following order: $CF_2=CCl_2 > CClF=CCl_2 > CClF=CClF \fallingdotseq CF_2=CClF > CF_2=CF_2$. This trend can be rationalized by considering the relative stability of the intermediate biradicals (see below) and steric factors. The indene dimer was a main by-product, obtained as a high-boiling residue. Tarry polymeric products were also generated, especially in the case of TFE, CTFE and *unsym*-DCDFE.

In thermal cycloadditions, it has been known[1] that a structual requirement for the fluoro olefins is the presence of a terminal difluoromethylene group. Fluoro olefins such as TFE, CTFE, and *unsym*-DCDFE undergo thermal cycloaddition to form cyclobutanes with themselves and other unsaturated compounds,

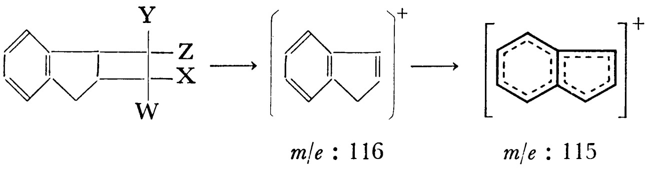
TABLE 1. PHOTO-SENSITIZED ADDITION REACTION OF INDENE TO CHLOROFLUORO OLEFINS

Chlorofluoro olefin		Indene	PhCOPh	$CF_2ClCFCl_2$	Method[a)]	Irrad. time	Conversion of indene	Yield[b)]	High-boiling product
	mol	mol	mol	mol		h	%	%	g
$CClF{=}CCl_2$	0.50	0.10	0.01	1.00	A	168	62.9	65.3	2.4
$CClF{=}CClF$	0.50	0.10	0.01	1.00	A	168	64.7	63.3	2.1
$CF_2{=}CCl_2$	0.50	0.10	0.01	1.00	A	168	98.3	57.6	3.8
$CF_2{=}CClF$	0.50	0.10	0.01	1.00	A	168	69.8	54.5	3.5
$CClF{=}CCl_2$	0.50	0.10	0.01	—	B	168	69.8	61.5	3.1
$CClF{=}CCl_2$	0.50	0.10	0.01	1.00	C	20	100	85.1	2.1
$CClF{=}CClF$	0.50	0.10	0.01	1.00	C	20	98.3	62.5	3.5
$CF_2{=}CCl_2$	0.50	0.10	0.01	1.00	C	8	97.4	84.1	2.1
$CF_2{=}CF_2$	0.50	0.10	0.01	1.50	D	20	94.0	4.9	12.8

a) Methods A and B: The reaction carried out in a Pyrex ampoule. Methods C and D: The reaction carried out by using an immersion well photo-reactor. b) The yields were calculated by the amounts of indene consumed.

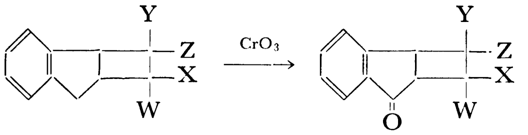
but *sym*-DCDFE and TCFE do not cycloadd thermally. In contrast, there is no such a structural requirement in the photo-cycloaddition with indene. All chlorofluoroethylenes examined gave the corresponding cycloadducts. Thermal cycloaddition of indene has not been known.

The structures of the cycloadducts were elucidated by means of their elemental analyses, 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 formed by the cleavage of four-membered ring shown as follows:



The presence of several stereoisomers of the cycloadducts was indicated in ^{19}F NMR spectra. The stereoisomers could not be separated by distillation or GLC. However, partial separation was achieved by fractional crystallization. The ratio of the isomers calculated from the intensity of ^{19}F NMR spectra are shown in Table 2 together with their ^{19}F chemical shifts.

The configurations of the stereoisomers were assigned by means of NMR spectra of their oxidized products. The cycloadducts (**1**—**5**) were oxidized by chromium trioxide to give the corresponding 6,6,7,7-tetrahalogeno-2,3-benzobicyclo[3.2.0]hept-2-en-4-ones (**6**—**10**).



1—**5** **6**—**10**

In addition to the more easily interpreted NMR of these oxidized products, **6**—**10**, they are more easily crystallized due to the presence of the carbonyl group. The assignments of configuration of the stereoisomers, estimated from the values of chemical shifts, coupling constants and nuclear Overhauser effect (NOE) are shown in Table 3 together with ^{19}F chemical shifts.

TABLE 2. THE ISOMER RATIOS AND FLUORINE-19 CHEMICAL SHIFTS OF THE CYCLOADDUCTS

Compound	Isomer ratio	Fluorine-19 chemical shifts/ppm			
		W	X	Y	Z
1a	38	F 29.8	Cl	Cl	Cl
1b	46	Cl	F 5.3	Cl	Cl
1c	6	Cl	Cl	F 20.1	Cl
1d	10	Cl	Cl	Cl	F 11.8
2a	30	F 36.0	Cl	F 20.6	Cl
2b	12	F 45.0	Cl	Cl	F 36.2
2c	37	Cl	F 11.9	F 25.0	Cl
2d	21	Cl	F 30.9	Cl	F 25.6
3a	100	F 29.6	F 12.9	Cl	Cl
3b	0	Cl	Cl	F —	F —
4a	48	F 41.9	F 16.0	F 40.9	Cl
4b	52	F 33.1	F 27.4	Cl	F 37.9
4c	0	F —	Cl	F —	F —
4d	0	Cl	F —	F —	F —
5	100	F 44.6	F 30.1	F 35.4	F 35.4

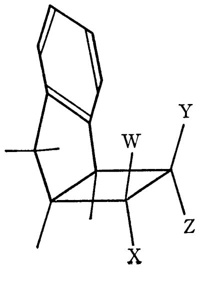
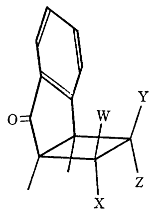
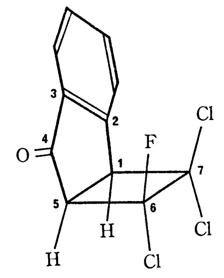


Table 3. Fluorine-19 chemical shifts and melting points of the oxidized products of the cycloadducts

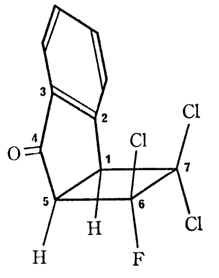
Compound	Fluorine-19 chemical shifts/ppm				Mp
	W	X	Y	Z	°C
6a	F 20.3	Cl	Cl	Cl	132.1
6b	Cl	F 7.7	Cl	Cl	119.6
6c	Cl	Cl	F 16.6	Cl	not isol.
6d	Cl	Cl	Cl	F 11.3	not isol.
7a	F 26.7	Cl	F 19.8	Cl	113.4
7b	F 36.0	Cl	Cl	F 33.4	110.6
7c	Cl	F 14.4	F 21.7	Cl	114.3
7d	Cl	F 30.9	Cl	F 27.7	not isol.
8a	F 19.6	F 12.6	Cl	Cl	96.6
9a	F 31.8	F 15.6	F 37.7	Cl	94.8
9b	F 23.1	F 26.8	Cl	F 37.4	64.6
10	F 34.6	F 29.9	F 32.6	F 34.8	86.8



Thus, the resonance peak of fluorine of **6a** is shifted 9.5 ppm down-field from that of **1a**. The shift is due to the electric field effect of the neighboring carbonyl group. On the other hand, ^{19}F chemical shift of **6b** did not differ from that of **1b**. Similar shifts are observed only for the fluorines in the W position of other isomers. When the fluorine nucleus of **6b** was irradiated, the integral intensity of hydrogen on the 5 position increased (14%). However, no NOE was observed in the other isomer, **6a**. Similarly, for the other isomers, when the fluorine nucleus in the X position was irradiated, the integral intensity of hydrogen on the 5 position increased (more than 10%), and irradiation of fluorine in the Z position increased (10%) that of hydrogen on the 1 position. The NMR of the series of the compounds (**6**—**10**) will be reported elsewhere in more detail.[7]



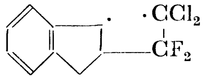
6a



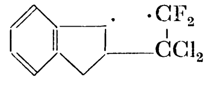
6b

As shown in Table 2, the distribution of the stereoisomers reflects good regioselectivity and poor stereoselectivity of the reaction. In the addition of TCFE, four cycloadducts, **1a**, **1b**, **1c**, and **1d**, were obtained in the ratio of 38:46:6:10. Two isomers (**1a** and **1b**) with a fluorine on the 6 position were obtained in higher yields than the other two isomers (**1c** and **1d**) with a fluorine on the 7 position. The reaction thus shows a minimum of 84% regioselectivity. In the case of *unsym*-DCDFE, only one isomer (**3a**) with two fluorines on the 6 position was formed, and the other isomer (**3b**) was not detected. From CTFE, two isomers (**4a** and **4b**) with a chlorine on the 7 position were obtained in the ratio of 52:48, but the other two isomers (**4c** and **4d**) were not detected. *unsym*-DCDFE and CTFE show complete regioselectivity in the reactions. *sym*-DCDFE gave four stereoisomers, **2a**, **2b**, **2c** and **2d**, in the ratio of 30:12:37:21.

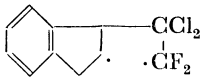
The observed results for these photo-cycloadditions may be explained by a mechanism in which biradical intermediates are formed as shown below in the case of *unsym*-DCDFE.



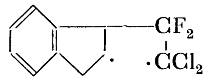
I



II



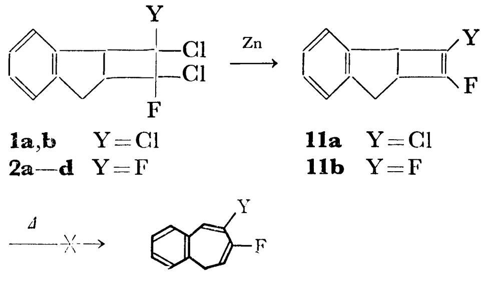
III



IV

A triplet state-excited indene would attack the *unsym*-DCDFE and four different biradicals might be generated as intermediates. These would lead to the cycloadducts by intramolecular coupling. Since the stabilities of halogenated carbon radicals follow the order: $\cdot CCl_2 > \cdot CClF \gg \cdot CF_2$, and the benzyl type radicals (I and II) are more stable than III and IV, the intermediate I would be formed preferentially to give **3a**. Presumably, the stereochemistry of this cycloaddition is mainly controlled by the stabilities of the intermediate biradicals. Other cofactors might be steric effects and fluorine hyperconjugation which has been proposed as an important factor in the increased amount of ring closure of the intermediate biradicals.[6]

The cycloadducts (**1a**, **b**, and **2a**—**d**) were dechlorinated with zinc powder and the corresponding cyclic olefins (**11a**, **b**) were obtained in high yields. Dechlorination of **2a**—**d** is more difficult than for **1a**,**b**

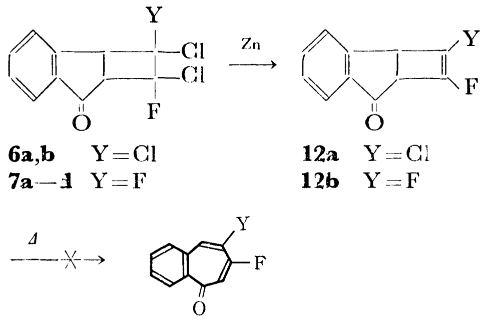


1a,**b** Y=Cl
2a—**d** Y=F
11a Y=Cl
11b Y=F

with only 15% of **2a**—**d** being dechlorinated under the conditions used for **1a,b**. Higher reaction temperature (140 °C) was required for complete dechlorination of **2a**—**d**.

The thermal ring expansion reaction of **11a** and **11b** did not occur at 200 °C. This is in accordance with the Woodward-Hoffmann's rule which predicts that the thermal cleavage of cyclobutenes will occur in a conrotatory fashion. In the case of **11a** and **11b**, which have the cyclobutene ring fused to the five membered ring, the conrotatory cleavage would lead to the sterically untenable *trans*-cycloheptatriene.

Similarly, the cyclic ketones (**6a,b** and **7a**—**d**) obtained from oxidation of the cycloadducts (**1a,b** and **2a**—**d**) gave the corresponding olefins (**12a,b**) by dechlorination with zinc. Longer reaction time was required for the dechlorination of **7a**—**d**. Upon heating **12a** and **12b** at 200 °C, thermal ring expansion to benzotropone again did not occur.



The cycloadduct (**3a**) was brominated with *N*-bromosuccinimide to give the monobromide (**13a**) almost quantitatively. The NMR signal of the hydrogen on the 4 position appears as a singlet at 5.51 ppm being shifted downfield by the geminal bromine. The singlet peak reflects a small H^4–H^5 coupling constant (less than 1 Hz). From the Karplus' relationship between vicinal H-H coupling constants and dihedral angles, H^4 is considered to be on the opposite side of the five membered ring plane from H^5. Hence, bromine substitution occurred on the sterically favorable position of the methylene group with high selectivity.

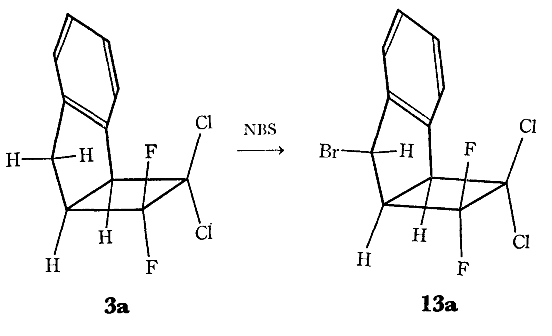
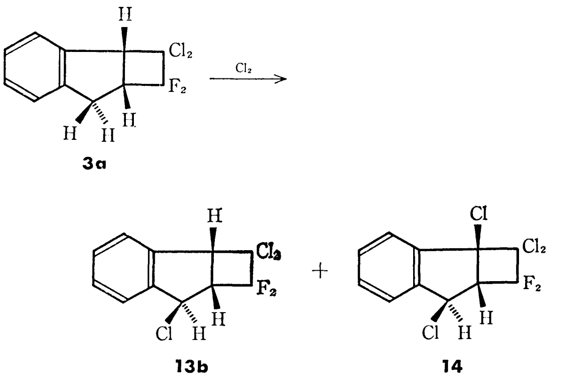
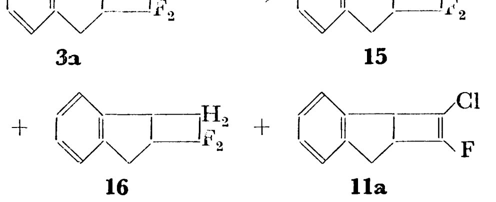


Photo-chlorination of **3a** afforded the monochloride (**13b**) in 84.4% yield together with a small amount (6.3% yield) of the dichloride (**14**). Similar to bromination, the same hydrogen was replaced by chlorine in the first step with further chlorination taking place on the 1 position.



Reduction of **3a** with lithium aluminum hydride afforded **15**, **16** and **11a**, which presumably resulted from the elimination of hydrogen fluoride from **15**.



Experimental

The melting points were determined on a 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 a Hitachi Model R-22 apparatus (90 MHz) using TMS as an internal standard for ^{1}H, and on a Model R-20 B apparatus (56.45 MHz) using trifluoroacetic acid as an external standard for ^{19}F.

Materials. Commercially available indene was used after distillation under an argon atmosphere. The chlorofluoroethylenes were prepared by dechlorination from the corresponding chlorofluoroethanes.

Trichlorofluoroethylene (TCFE): Dechlorination of pentachlorofluoroethane by zinc powder in ethanol gave TCFE, which was distilled through 50 cm column packed with glass helices (bp 71—72 °C).

*1,1-Dichloro-2,2-difluoroethylene (*unsym*-DCDFE)*: 1,1,1,2-Tetrachloro-2,2-difluoroethane was prepared by the isomerization of 1,1,2,2-tetrachloro-1,2-difluoroethane using aluminum trichloride catalyst.[8] Dechlorination of 1,1,1,2-tetrachloro-2,2-difluoroethane gave *unsym*-DCDFE (bp 18—19 °C).

*1,2-Dichloro-1,2-difluoroethylene (*sym*-DCDFE) and Chlorotrifluoroethylene (CTFE)*: Dechlorination of 1,1,2,2-tetrachloro-1,2-difluoroethane and 1,1,2-trichloro-1,2,2-trifluoroethane gave *sym*-DCDFE (bp 19—20 °C) and CTFE (bp −26—27 °C), respectively.

Tetrafluoroethylene (TFE): TFE was prepared by debromination of 1,2-dibromotetrafluoroethane with zinc and introduced into a photo-reator immediately.

Photo-cycloaddition. Photo-cycloadditions were carried out using four different reaction conditions (Method A, B, C, and D). A typical procedure is described for each Method.

Method A; Reaction of Indene and Trichlorofluoroethylene (TCFE): A solution of indene (11.6 g, 0.100 mol), TCFE

TABLE 4. MELTING POINTS AND ANALYTICAL DATA OF THE CYCLOADDUCTS AND THEIR DERIVATIVES

Compound	Mp[a)] °C	Formula	C% Found	C% Calcd	H% Found	H% Calcd
1a	101.3	$C_{11}H_8Cl_3F$	49.44	49.76	3.02	3.04
1b	81.1	$C_{11}H_8Cl_3F$	49.83	49.76	3.10	3.04
2a	111.9	$C_{11}H_8Cl_2F_2$	52.85	53.04	3.16	3 24
2b	86.3	$C_{11}H_8Cl_2F_2$	52.56	53.04	3.04	3.24
2c	65.3	$C_{11}H_8Cl_2F_2$	53.13	53.04	3.24	3.24
3a	74.3	$C_{11}H_8Cl_2F_2$	52.74	53.04	3.29	3.24
5	55.1	$C_{11}H_8F_4$	61.01	61.12	3.75	3.73
6a	132.1	$C_{11}H_6OCl_3F$	47.33	47.27	2.15	2.16
6b	119.6	$C_{11}H_6OCl_3F$	47.53	47.27	2.23	2.16
7a	113.4	$C_{11}H_6OCl_2F_2$	50.34	50.22	2.58	2.30
7b	100.6	$C_{11}H_6OCl_2F_2$	50.13	50.22	2.24	2.30
7c	114.3	$C_{11}H_6OCl_2F_2$	50.05	50.22	2.11	2.30
8a	96.6	$C_{11}H_6OCl_2F_2$	50.07	50.22	2.18	2.30
9a	94.8	$C_{11}H_6OClF_3$	53.38	53.57	2.37	2.45
9b	64.6	$C_{11}H_6OClF_3$	53.69	53.57	2.45	2.45
10	86.8	$C_{11}H_6OF_4$	57.06	57.40	2.65	2.63
11a	oil	$C_{11}H_8ClF$	67.91	67.88	4.13	4.14
11b	oil	$C_{11}H_8F_2$	74.05	74.15	4.23	4.53
12a	58.2	$C_{11}H_6OClF$	63.05	63.33	2.90	2.90
12b	oil	$C_{11}H_6OF_2$	67.81	68.75	3.23	3.15
13a	oil	$C_{11}H_7BrCl_2F_2$	40.42	40.28	2.32	2.15
13b	oil	$C_{11}H_7Cl_3F_2$	46.49	46.60	2.44	2.49
14	84.4	$C_{11}H_6Cl_4F_2$	41.45	41.55	1.91	1.90
15	136.2	$C_{11}H_9ClF_2$	61.41	61.55	4.14	4.23

a) Recrystallized from ethanol.

(74.7 g, 0.500 mol) and benzophenone (1.8 g, 0.010 mol) in 1,1,2-trichlorotrifluoroethane (187 g, 1.00 mol) was sealed under an argon atmosphere in a 300 ml Pyrex ampoule, and irradiated with a 100 W high pressure mercury lamp at room temperature for 168 h. After recovery of the solvent and TCFE by distillation, the residue was distilled *in vacuo* to give indene (4.3 g, 38.1% recovered), a cycloadduct (10.9 g, 65.3% yield) boiling at 131 °C/4 mmHg and a high-boiling residue, which contained benzophenone. The cycloadduct crystallized after standing overnight. The ^{19}F NMR spectrum of the cycloadduct indicated that it consisted of four isomers, **1a**, **1b**, **1c**, and **1d**, in the ratio of 38:46:6:10. Two of these, **1a** and **1b**, were isolated by fractional recrystallization. Indene dimer was also isolated from the high-boiling residue as colorless needles (mp 109.5 °C).

Method B; *Reaction of Indene and Trichlorofluoroethylene (TCFE)*: A mixture of indene (11.6 g, 0.100 mol), TCFE (74.7 g, 0.500 mol) and benzophenone (1.8 g, 0.010 mol) was irradiated in a 100 ml Pyrex ampoule with a 100 W high pressure mercury lamp for 168 h. The product was separated by distillation to give indene (3.5 g, 30.2% recovered), a cycloadduct (11.4 g, 61.5% yield, bp 120—122 °C/3 mmHg) and a high-boiling residue (4.9 g).

Method C; *Reaction of Indene and Trichlorofluoroethylene (TCFE)*: A solution of indene (11.6 g, 0.100 mol), TCFE (74.7 g, 0.500 mol) and benzophenone (1.8 g, 0.010 mol) in 1,1,2-trichlorotrifluoroethane (187 g, 1.00 mol) was irradiated for 20 h in an immersion well Pyrex photo-reactor (300 ml capacity with a water-cooled 100 W mercury lamp) under an argon atmosphere. All indene was consumed and a cycloadduct (22.6 g, 85.1% yield) and a high-boiling residue (3.0 g) were obtained.

Method D; *Reaction of Indene and Tetrafluoroethylene (TFE)*: A solution of indene (11.6 g, 0.100 mol) and benzophenone (1.8 g, 0.010 mol) in 1,1,2-trichlorotrifluoroethane (280 g) was placed in a 300 ml immersion well Pyrex photo-reactor, and cooled in an ice bath. TFE, which was generated from the debromination reaction of 1,2-dibromotetrafluoroethane (130 g, 0.500 mol) and zinc (100 g) in ethanol, was bubbled and absorbed into the solution. Then the solution was irradiated as in Method C for 20 h. Distillation gave indene (0.7 g, 6.0% recovered), a cycloadduct (1.0 g, 4.9% yield, bp 60—65 °C/3 mmHg) and a high-boiling residue (12.8 g).

Oxidation of the Adducts. The cycloadducts (**1**—**5**) were oxidized with chromium trioxide to the corresponding ketones (**6**—**10**). The oxidation of 6,6,7,7-tetrafluoro-2,3-benzobicyclo[3.2.0]hept-2-ene (**5**) is described as a typical experimental procedure.

*6,6,7,7-Tetrafluoro-2,3-benzobicyclo[3.2.0]hept-2-en-4-one (**10**)*: To a solution of chromium trioxide (2.4 g, 24 mmol) in water (5 ml) was added a solution of **5** (1.3 g, 6 mmol) in acetic acid (15 ml) and the mixture was heated at reflux for 8 h. After cooling, the solution was poured into an ice-cooled aqueous sodium hydrogensulfite solution and was extracted with two 30 ml portions of ether. The combined extracts were dried over sodium sulfate and evaporated. The residue crystallized after standing overnight. Recrystallization of the product from ethanol gave **10** (1.3 g, 94.1% yield) as colorless columns: mp 86.8 °C.

Dechlorination. The cycloadducts (**1a**, **b** and **2a**—**d**) and ketones (**6a**, **b** and **7a**—**d**) obtained by oxidation were dechlorinated with zinc powder to the corresponding olefins (**11a**, **b** and **12a**, **b**). The following procedures are illustrative.

*7-Chloro-6-fluoro-2,3-benzobicyclo[3.2.0]hepta-2,6-diene (**11a**)*: To a solution of the mixture of the isomers (**1a** and **1b**, 2.7 g, 10 mmol) in absolute ethanol (40 ml) was added zinc powder (6.4 g). The mixture was heated at reflux with stirring for 8 h. After removal of solid material by filtration, the filtrate was poured into diluted hydrochloric acid and was extracted with three 50 ml portions of dichloromethane. The combined extracts were dried over magnesium sulfate and evaporated to give an oily residue (2.6 g). Further purification was effected by preparative GLC (at 100 °C using an aluminum column, 6 m long × 10 mm diameter, packed with Silicone DC-QFl-Chromosorb W) to give **11a** (1.7 g, 87.3% yield) as colorless oil: n_D^{20} 1.5509, d_4^{20} 1.251, IR $\nu_{C=C}$ 1705 cm^{-1}.

*6,7-Difluoro-2,3-benzobicyclo[3.2.0]hepta-2,6-diene (**11b**)*: The synthesis of **11b** from the mixture of isomers (**2a**—**d**, 2.5 g, 10 mmol) followed the procedure used with **1a** and **1b**, except that a higher reaction temperature (140 °C) was adopted using ethylene glycol (25 ml) as a solvent. The product (**11b**, 1.3 g, 73.0% yield) was obtained as a colorless oil: n_D^{20} 1.5183, IR $\nu_{C=C}$ 1764 cm^{-1}.

*7-Chloro-6-fluoro-2,3-benzobicyclo[3.2.0]hepta-2,6-dien-4-one (**12a**)*: The synthesis of **12a** from the mixture of isomers (**6a** and **6b**, 2.8 g, 10 mmol) followed the procedure used with **1a** and **1b**. The product (1.7 g, 81.5% yield) was obtained as colorless prisms (from ethanol): mp 58.2 °C, IR $\nu_{C=C}$ 1705 cm^{-1}, $\nu_{C=O}$ 1721 cm^{-1}.

*6,7-Difluoro-2,3-benzobicyclo[3.2.0]hepta-2,6-dien-4-one (**12b**)*: The synthesis of **12b** from the mixture of isomers (**7a**—**d**) followed the procedure used with **1a** and **1b**, except that the reaction time was prolonged to 18 h. The product (**12b**, 83.3% yield) was obtained as a colorless oil: d_D^{20} 1.5410, IR $\nu_{C=C}$ 1773 cm^{-1}, $\nu_{C=O}$ 1724 cm^{-1}.

Halogenation of the Adduct. Bromination with *N*-bromosuccinimide and photo-chlorination of a cycloadduct (**3a**) gave corresponding 4-halides (**13a** and **13b**).

*4-Bromo-7,7-dichloro-6,6-difluoro-2,3-benzobicyclo[3.2.0]hept-2-ene (**13a**)*: To a solution of **3a** (2.5 g, 10 mmol) in tetrachloromethane (30 ml), were added *N*-bromosuccinimide (1.8 g, 10 mmol) and a small amount of benzoyl peroxide (*ca.* 3 mg). The mixture was heated at reflux under an argon atmosphere for 2 h. The white precipitate generated was filtered off and the filtrate was evaporated to give a yellow oil. Further purification was effected by liquid chromatography (silica gel, tetrachloromethane as an eluting solvent) to give **13a** (3.2 g, 97.6% yield) as a colorless oil: n_D^{20} 1.5612.

*4,7,7-Trichloro-6,6-difluoro-2,3-benzobicyclo[3.2.0]hept-2-ene (**13b**) and 1,4,7,7-Tetrachloro-6,6-difluoro-2,3-benzobicyclo[3.2.0]-hept-2-ene (**14**)*: Chlorine (1.5 g, 20 mmol) was absorbed by bubbling through a solution of **3a** (2.5 g, 10 mmol) in tetrachloromethane (200 ml). The solution was exposed to sun light for 10 min until the yellow color disappeared. After removal of the solvent by evaporation, the residue was distilled under reduced pressure to give **13b** (2.4 g, 84.4% yield) as a slightly yellow oil: bp 115—116 °C/2 mmHg, n_D^{20} 1.5523. Purification of the higher boiling products by using the preparative GLC gave **14** (0.2 g, 6.3% yield) as colorless prisms (from ethanol): mp 84.4 °C.

Reduction of the Adduct. The cycloadduct (**3a**) was reduced with lithium aluminum hydride.

*7-Chloro-6,6-difluoro-2,3-benzobicyclo[3.2.0]hept-2-ene (**15**)*: To a solution of **3a** (2.5 g, 10 mmol) in absolute ether (100 ml) was added lithium aluminum hydride (1.2 g, 30 mmol) and the mixture was heated at reflux for 20 h with stirring. The mixture was poured into ice-cooled diluted sulfuric acid. The organic layer separated was dried over magnesium sulfate and evaporated. The residue crystallized after standing overnight. The product was recrystallized from ethanol to give **15** (1.1 g, 51.2% yield)as colorless plates: mp 136.2 °C. Analysis of the mother liquid by a mass spectrometer coupled with GC showed the existence of by-products, 6,6-difluoro-2,3-benzobicyclo[3.2.0]hept-2-ene (**16**) and 7-chloro-6-fluoro-2,3-benzobicyclo[3.2.0]hepta-2,6-diene (**11a**).

References

1) W. H. Sharkey, "Fluorine Chemistry Reviews," Marcel Dekker Inc., New York (1968), Vol. II, p. 1.

2) N. J. Turro and P. D. Bartlett, *J. Org. Chem.*, **30**, 1849 (1965); P. D. Bartlett, B. M. Jacobson, and L. E. Walker, *J. Am. Chem. Soc.*, **95**, 146 (1973); P. D. Bartlett and J. J. B. Mallet, *J. Am. Chem. Soc.*, **98**, 143 (1976).

3) D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Commun.*, **1969**, 800; B, Sket and M. Zupan, *J. Chem. Soc., Chem. Commun.*, **1976**, 1053; **1977**, 365; D, Bryce-Smith, A. Gilbert, B. H. Orger, and P. J. Twitchett, *J. Chem. Soc., Perkin Trans. 1*, **1978**, 243.

4) A. J. Wexler and J. S. Swenton, *J. Am. Chem. Soc.*, **98**, 1602 (1976); M. L. Greenlee, E. L. Fritzen, Jr., and J. S. Swenton, *J. Org. Chem.*, **43**, 4512 (1978).

5) H. Kimoto, H. Muramatsu, and K. Inukai, *J. Fluorine Chem.*, **9**, 417 (1977) and references cited therein.

6) P. J. Wagner and M. J. Thomas, *J. Am. Chem. Soc.*, **98**, 241 (1976).

7) K. Takahashi, H. Kimoto, and H. Muramatsu, manuscript in preparation.

8) K. Okuhara, *J. Org. Chem.*, **41**, 1487 (1976).