

Received: June 9, 1978

2,2'-DIHALO-BIS(PERFLUOROCYCLOALKENES): PART 1. SYNTHESIS

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SUMMARY

An improved synthesis of 1-chloro-2-iodo-perfluorocycloalkenes and their copper coupled products, 2,2'-dichloro-bis(perfluorocycloalkenes) is reported. Mixtures of equal molar quantities of different chloriodoperfluorocycloalkenes react with copper to give predominately the mixed coupled product. For example, 1-chloro-2-iodoperfluorocyclobutene and 1-chloro-2-iodoperfluorocyclopentene react with copper to give 2-chloro-1-[1'-2'-chlorohexafluorocyclopentenyl]-tetrafluorocyclobutene in 70% yield. The 2,2'-dichloro-bis(perfluorocycloalkenes) react with potassium iodide in DMF to substitute one or both vinylic chlorine atoms by iodine. Copper coupling of 2,2'-diiodo-bis(perfluorocyclopentene) gives the cyclic tetramer perfluorotetracyclopentenocyclo-octatetraene, whereas 2-chloro-2'-iodo-bis(perfluorocyclopentene) and copper gives the linear tetramer 2,2''-dichloro-tetrakis(perfluorocyclopentene).

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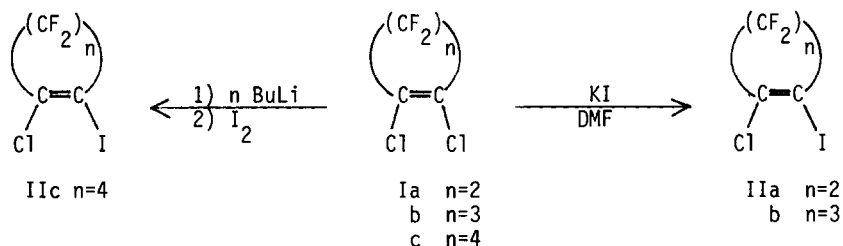
## INTRODUCTION

Literature on the chemistry of 2,2'-dichloro-bis(perfluorocycloalkenes) is limited to a single report by Cullen et al [1]. We would like to now report on our studies of this novel class of compounds and in this paper present an improved synthesis of a variety of simple and mixed 2,2'-dichloro-bis(perfluorocycloalkenes) and their reaction with potassium iodide in DMF solution. Future papers will report on the products obtained from reactions with mono and difunctional primary and secondary amines, hydrazine and certain glycols.

In a previous report we described the reaction of various alkali halides with 1,2-dichloroperfluorocycloalkenes in low polarity and high polarity solvents [2]. These initial studies pointed out the distinct advantages of high polarity solvents, specifically, improved yields and shorter reaction times. Some control over the relative amounts of mono and disubstituted products was afforded by changing the alkali halide/perfluorocycloalkene ratio. However, the yield of monosubstituted products was generally poor, 36% for 1-chloro-2-iodoperfluorocyclobutene (IIa), 45% for 1-chloro-2-iodoperfluorocyclopentene (IIb) and 26% for 1-chloro-2-iodoperfluorocyclohexene (IIc).

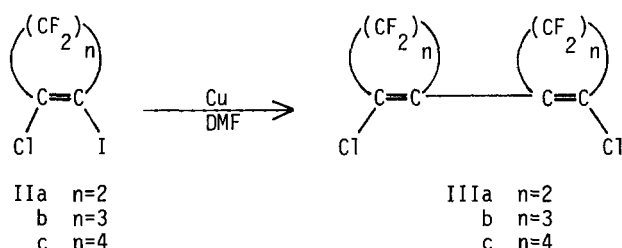
## RESULTS AND DISCUSSIONS

The preparation of chloriodoperfluorocycloalkenes (IIa and IIb) was significantly improved by conducting the reaction at temperatures lower than previously reported [2]. These results would suggest that the energy of activation for replacement of the second vinylic chlorine is increased by replacement of the first chlorine atom by iodine. Conversion of Ia and Ib to the corresponding diiodides at the lower temperature was minimal.



Preparation of IIC by the KI/DMF method is difficult and proceeded in low yield. An 80% yield of IIC was obtained by converting IC to the lithio salt at  $-75^{\circ}$  and then addition of iodine.

Following the disclosure of Tatlow et. al. [3] we have shown that copper powder served as an effective reagent for the coupling of iodoperfluorocycloalkenes [4, 5] to principally cyclic perfluorinated derivatives. One may compare these results with those reported by Camaggi [6] who found both linear and cyclic products using copper bronze as the coupling agent. The coupling procedure reported in this paper provides a distinct improvement in yields over that reported previously.



The only by-product isolated from these reactions is the reduced product 2H,2'H-dodecafluoro-(bi-1-cyclopenten-1-yl). Similar reduced products are not found when the perfluorocycloalkenes were cyclobutene or cyclohexene.

Equal molar mixtures of two different chloriodoperfluorocycloalkenes reacted with copper to give the mixed coupled product in 50-70% yield (Table 1). A purely statistical distribution, of course, would have predicted 33% of each of the possible combinations.

TABLE 1

Copper Coupling Mixed 1-chloro-2-iodoperfluoroalkenes

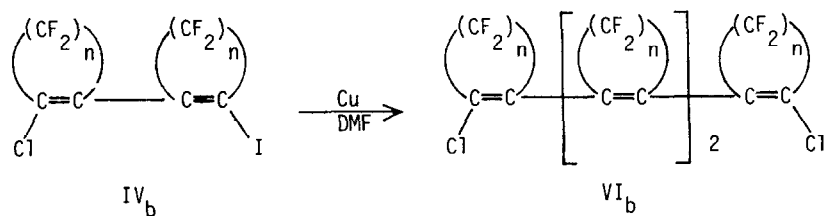
Reactants	Products* (isolated yield)			
	IIIa	IIIb	IIIc	III Mixed
IIa, IIC	30%	---	13%	57% (50%)
IIa, IIb	10%	20%	---	70% (70%)
IIb, IIC	---	30%	20%	50% (42%)

\*Product distribution was determined by VPC on crude mixture.

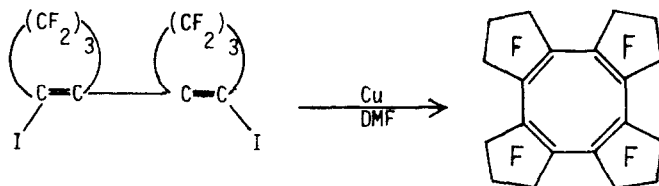
The 2,2'-dichloro-bis(perfluorocycloalkenes) IIIa and IIIb reacted readily with potassium iodide in DMF to replace one or both vinylic chlorine atoms. The facile nature of this reaction indicated, especially in the bis-perfluorocyclobutene case, that conjugation of the two double bonds afforded some stabilization of the intermediate anion. The reaction of IIIa with potassium iodide in diglyme was nearly quantitative within 2 hours at room temperature yielding only 2,2'-diiodo-bis(perfluorocyclobutene).

Molecular models clearly show that steric constraints on 2,2'-dichloro-bis(perfluorocyclohexene) (IIIc) prevent the molecule from lying with the double bonds coplanar. Thus, it was not surprising to observe that IIIc and IIC were similar in reactivity. The best method for replacement of vinylic chlorine in IIIc involved the conversion to the lithio salt with butyl lithium and subsequent reaction with iodine.

Copper coupling of 1-chloro-2'-iodo-bis(perfluorocyclopentene) afforded an excellent yield of the linear tetramer VIb.



Similarly, copper coupling of 2,2'-diiodo-bis(perfluorocyclopentene) (Vb) gave a 91% yield of the colorless cyclic tetramer VIIb. The cyclic tetramer VIIb has also been prepared by the reaction of copper with 1,2-diiodoperfluorocyclopentene [5].



## EXPERIMENTAL

All melting points were determined in sealed capillary tubes and are uncorrected. UV spectra were obtained on a Cary Model 17 spectrophotometer. NMR  $^{19}\text{F}$  spectra were obtained on a Varian HA-100 spectrometer using  $\text{CCl}_3\text{F}$  as an internal standard. Mass spectral analysis were obtained on an Atlas CH-4 using 70 ev as the ionization potential. Chromatographic analysis used 20% SF-1265(Qf-1) on Chromosorb W for VPC column packing. Chemical analysis were performed by Huffman Laboratories at Wheatridge, Colorado.

The chemicals used in this study were reagent grade and were carefully dried prior to reaction. Catalytic activity of the copper powder varied with grade and manufacturer; however, best results were obtained with pure copper powder from Matheson (CX-1925) or dry freshly precipitated copper from a solution of copper sulfate and zinc dust.

Preparation of 1-chloro-2-iodotetrafluorocyclobutene (IIa)

Finely ground potassium iodide (332g, 2.0 mol) and 1.0 l of dry DMF were stirred at room temperature until all solids were dissolved. To the solution was added dropwise 194g (1.0 mol) of Ia and the resulting mixture maintained at  $55\text{-}60^\circ$  for 19 h. A Barrett trap was fitted between the flask and the condenser and 300 ml of water added to the reaction mixture. The reaction mixture was heated to reflux and a heavy organic layer periodically removed from the bottom of the trap. The organic layer was washed repeatedly with water, dried over magnesium sulfate, then fractionally distilled yielding 215g (75%) of IIa, b.p.  $56^\circ/97$  mm (lit., [2] b.p.  $54^\circ/100$ mm) and 38g (10%) of 1,2-diiodotetrafluorocyclobutene, b.p.  $93^\circ/97$ mm. (lit., [2] b.p.  $95^\circ/100$ mm)

Preparation of 1-chloro-2-iodohexafluorocyclopentene(IIb)

In a manner similar to that described above, 332g (2.0 mol) of KI, 1.0 l of DMF and 244g (1.0 mol) of Ib were mixed and heated to  $90^\circ$  for 19 h then at  $125^\circ$  for 2 h. Workup of the reaction mixture, as above, gave 286g (85%) of IIb, b.p.  $60^\circ/97$  mm and 25g (10%) of unreacted Ib (lit., [2] b.p.  $62^\circ/100$  mm).

Preparation of 1-chloro-2-iodooctafluorocyclohexene (IIc)

A stirred solution of 20g (0.068 mol) of Ic in 100 ml of ether was cooled to  $-75^{\circ}$  by solid  $\text{CO}_2$ -acetone bath then 32 ml of n-butyllithium (2.2M in hexane) was added dropwise from a syringe. The reaction mixture was held at  $-75^{\circ}$  for 30 min. then 25.4g (0.10 mol) of iodine was added and the mixture allowed to warm to room temperature slowly. The reaction mixture was poured into water and the organic layer was removed and subsequently washed with sodium bisulfite solution, water, dried over  $\text{MgSO}_4$  and concentrated in a rotary evaporatory. Distillation of the dark residue gave 21.0g (80%) of IIc, b.p.  $79-80^{\circ}$  /69mm (lit., [2] b.p.  $142^{\circ}$  /630mm).

Reaction of IIa with copper powder

Into a 50 ml round bottom flask fitted with a modified Friedrichs condenser was added 80.0g of copper powder, 20.0g (0.07 mol) of IIa, 18 drops of DMF and a magnetic stirring bar. After heating the stirred reaction mixture to  $130^{\circ}-135^{\circ}$  for 4.5 h the resulting thick slurry was sublimed under reduced pressure (yielding 9.0g (80%) of 2,2'-dichlorooctafluoro-(bi-1-cyclobuten-1-yl) (IIIa): m.p.  $69^{\circ}$  ; IR (KBr pellet)  $1575\text{ cm}^{-1}$  (C=C); UV  $\lambda$  max. (95% EtOH)  $209\text{ }\mu\text{m}$  ( $\epsilon$  2,500),  $268\text{ }\mu\text{m}$  ( $\epsilon$  7,500),  $260\text{ }\mu\text{m}$  ( $\epsilon$  10,200) (lit., [5] m.p.  $69.5-70.5^{\circ}$  ; IR (KBr)  $1575\text{ cm}^{-1}$  (C=C) ).

Reaction of IIb with copper powder

In a manner similar to that described above, 80.0g of copper powder, 20.0g (0.048 mol) of IIb and 18 drops of DMF were heated to  $130-135^{\circ}$  for 5.5 h. The resulting white slurry was extracted with ether and the ether extracts washed with water, dried over  $\text{MgSO}_4$  and distilled yielding 8.1g (81%) of 2,2'-dichlorododecafluoro-(bi-1-cyclopenten-1-yl) (IIIb): b.p.  $84-86^{\circ}$  /59mm; IR  $1650$  and  $1605\text{ cm}^{-1}$  (C=C); UV  $\lambda$  max. (95% EtOH)  $222\text{ }\mu\text{m}$  ( $\epsilon$  6,300),  $240\text{ }\mu\text{m}$  ( $\epsilon$  4,000); (lit., [5] b.p.  $148.5-149^{\circ}$  /618mm; IR (neat)  $1620$  (weak)  $\text{cm}^{-1}$ ) and 1.0g (12%) of 2H,2'H-dodecafluoro-(bi-1-cyclopenten-1-yl) IIIbH: m.p.  $83^{\circ}$  ; IR (KBr)  $1600\text{ cm}^{-1}$  (lit., [5] m.p.  $83-85^{\circ}$  ; IR (KBr)  $1618\text{ cm}^{-1}$ ).

### Reaction of IIc with copper powder

In a manner similar to that described above, 20.0g of copper powder, 5.0g (0.013 mol) of IIc and 4 drops of DMF were heated to 140-145° for 2 h. The reaction mixture was extracted with ether, and the ether extracts were washed with water, dried and concentrated. The crystalline residue was recrystallized from *n*-hexane yielding 3.0g (90%) of 2,2'-dichlorohexadecafluoro-(bi-1-cyclohexen-1-yl) (IIIc): m.p. 51°; IR (KBr) 1640 and 1610  $\text{cm}^{-1}$  (C=C); UV  $\lambda_{\text{max}}$ . 282  $\mu\text{m}$  ( $\epsilon$  1,630) and 205  $\mu\text{m}$  ( $\epsilon$  11,900) (lit., [5] m.p. 51.5-52.0°; IR (KBr) 1653 and 1626  $\text{cm}^{-1}$ ).

### Reaction of IIa and IIc with copper powder

A mixture of 2.86g (0.01 mol) of IIa, 3.86g (0.01 mol) of IIc, 25g of copper powder and 7 drops of DMF was stirred and heated to 135° for 5 h. The reaction mixture was extracted with ether then the combined ether extracts were washed with water, dried over  $\text{MgSO}_4$  and concentrated under vacuum. VPC analysis of the crude residue showed that it consisted of IIIa (30%), IIIc (13%) and an intermediate peak (57%).

Vacuum distillation of the crude residue gave 2.1g (50%) of a clear liquid with a VPC retention time identical to the intermediate peak. The liquid was identified as 2-chloro-1-[1'-(2'-chlorooctafluorocyclohexenyl)]-tetrafluorocyclobutene (IIIac): b.p. 86° /58 mm; refractive index (25°) 1.3832; IR (neat) 1670, 1640, 1580, 1200, 1055, 934, 875, 770 and 730  $\text{cm}^{-1}$ ;  $\text{NMR}^{19\text{F}}$  110.7 (2F), 113.9 (4F), 119.6 (2F) and 134.7 (4F) p.p.m.; UV  $\lambda_{\text{max}}$  (95% EtOH) 264  $\mu\text{m}$  ( $\epsilon$  14,800); mass spectrum  $\text{M}^+(2\text{Cl})$  418 and fragment ions 399 ( $\text{M}^+\text{F}$ ), 383 ( $\text{M}^+\text{-Cl}$ ), 349 ( $\text{M}^+\text{-CF}_3$ ) and 333 ( $\text{M}^+\text{-CF}_2\text{Cl}$ ). Calcd. for  $\text{C}_{10}\text{F}_{12}\text{Cl}_2$  : Cl, 16.14; Found: Cl, 15.22.

### Reaction of IIa and IIb with copper powder

Copper powder (25g), 2.86g (0.01 mol) of IIa, 3.36g (0.01 mol) of IIb and 7 drops of DMF were reacted and the products isolated in a manner similar to that described above. VPC analysis of the crude products (5.0g) showed that it consisted of IIIa (10%), IIIb (20%) and the mixed coupled product 2-chloro-1-[1'-(2'-chlorohexafluorocyclopentenyl)]-tetrafluorocyclobutene nc

(IIIab) (70%). Distillation gave 3.0g (70%) of IIIab : b.p.  $69^{\circ}$  /30 mm ; refractive index ( $25^{\circ}$ ) 1.3687; IR (neat) 1640, 1600, 1560, 1330, 1260, 1200, 1150, 1100, 1040, 930, 896, 875, 853 and  $754\text{ cm}^{-1}$ ; NMR  $^{19}\text{F}$  110.6 (2F), 112.0 (2F), 116.8 (2F), 117.6 (2F), 131.2 (2F) and 132.0 p.p.m. (2F); UV  $\lambda_{\text{max}}$  (95% EtOH)  $265\ \mu\text{m}$  ( $\epsilon$  12,300) and  $275\ \mu\text{m}$  ( $\epsilon$  11,400) ; mass spectrum  $\text{M}^+$  (2 Cl) 368 with fragment ions 349 ( $\text{M}^+-\text{F}$ ), 333 ( $\text{M}^+-\text{Cl}$ ), 299 ( $\text{M}^+-\text{CF}_3$ ), 283 ( $\text{M}^+-\text{CF}_2\text{Cl}$ ) and 249 ( $\text{M}^+-\text{C}_2\text{F}_5$ ). Calcd. for  $\text{C}_9\text{F}_{10}\text{Cl}_2$  : Cl, 19.02. Found: Cl, 18.80

#### Reaction of I Ib and I Ic with copper powder

Copper powder (25g), 3.36g (0.01 mol) of I Ib, 3.86g (0.01 mol) of I Ic and 7 drops of DMF were reacted and the products isolated as described above. VPC analysis of the crude product 6.0g showed that it consisted of IIIb (30%), IIIc (20%) and the mixed coupled product 2-chloro-1-[1'-(2'-chlorooctafluorocyclohexenyl)]-hexafluorocyclopentene nc (IIIbc) (50%). Distillation of the yellow oil gave 2.0g (42%) of IIIbc : b.p.  $61^{\circ}$  /29 mm; refractive index ( $25^{\circ}$ ) 1.3774; IR (neat) 1650, 1620, 1318, 1280, 1225, 1200, 1160, 1120, 1030, 980, 930, 875, 858 and  $710\text{ cm}^{-1}$ ; NMR  $^{19}\text{F}$  108-138 p.p.m. (complex); UV  $\lambda_{\text{max}}$ . (95% EtOH)  $205\ \mu\text{m}$  ( $\epsilon$  11,000) ; mass spectrum  $\text{M}^+$ (2 Cl) 468 with fragment ions 449 ( $\text{M}^+-\text{F}$ ), 433 ( $\text{M}^+=\text{Cl}$ ), 418  $\text{M}^+-\text{CF}_2$ ) 399 ( $\text{M}^+-\text{CF}_3$ ) and 383 ( $\text{M}^+-\text{CF}_2\text{Cl}$ ). Calcd for  $\text{C}_{11}\text{F}_{14}\text{Cl}_2$  : Cl. 14.95 Found: Cl, 14.80

#### Reaction of IIIa with Potassium Iodide (1:1 ratio)

A soln. of 1.80g (0.0108 mol) of KI in 12 ml of DMF was added to a stirred soln. of 3.16g (0.010 mol) of IIIa in 25 ml of DMF at room temperature. The reaction was stirred for an additional 5 h then poured into water. The resulting yellow ppt. was filtered, washed with water and fractionally sublimed yielding 0.5g of unreacted IIIa and 3.3g (80%) of 2-chloro-2'-iodooctafluoro-(bi-1-cyclobuten-1-yl) nc (IVa) : m.p.  $81^{\circ}$  ; IR (KBr) 1540, 1310, 1240, 1150 and  $875\text{ cm}^{-1}$ ; mass spectrum ( $\text{m}^+$ ) 410 (1 Cl) and fragment ions 391 ( $\text{M}^+-\text{F}$ ), 375 ( $\text{M}^+-\text{Cl}$ ), 341 ( $\text{M}^+-\text{CF}_3$ ), 310 ( $\text{M}^+\text{C}_2\text{F}_4$ ) and 283 ( $\text{M}^+-\text{I}$ ).



Reaction of IIIa with Potassium Iodide (1:3 ratio)

A mixture of 3.18g (0.10 mol) of IIIa, 5.0g (0.030 mol) of KI in 25 ml of diglyme was stirred at room temperature for 2 h then poured into water and extracted with ether. The ether extracts were washed with water, dried over  $MgSO_4$  and concentrated to a crystalline residue. The residue was recrystallized from *n*-hexane giving 4.5g (90%) of 2,2'-difiodooctafluoro-(bi-1-cyclobuten-1-yl) nc (Va) m.p. 148-148.5 ; IR (KBr) 1520, 1370, 1300, 1230, 1110, 820 and 760  $cm^{-1}$  ; NMR  $^{19}F$  105.6 (4F) singlet and 108.6 (4F) p.p.m. singlet ; UV  $\lambda_{max}$ . (95% EtOH) 320  $\mu m$  ( $\epsilon$  6,500), 292  $\mu m$  ( $\epsilon$  15,700), 270  $\mu m$  ( $\epsilon$  14,700) and 230  $\mu m$  ( $\epsilon$  9,200) ; mass spectrum  $M^+$  502 and fragment ions 483 ( $M^+-F$ ), 375 ( $M^+-I$ ), 356 ( $M^+-FI$ ), 325 ( $M^+-CF_2I$ ) and 248 ( $M^+-2I$ ).

Reaction of IIIb with Potassium Iodide (ambient)

A solution of 6.7g (0.04 mol) of KI in 25 ml of DMF was added to a mixture of 8.36g (0.02 mol) of IIIb in 10 ml of DMF at room temperature. The reaction mixture was stirred at room temperature for 16 h then poured into water and extracted with ether. The ether extracts were washed with water, dried over  $MgSO_4$  then concentrated under vacuum. The liquid residue was vacuum distilled yielding 9.4g (92%) of 2-chloro-2'-iododecafluoro-(bi-1-cyclopenten-1-yl) nc (IVb) ; b.p. 97-99 $^{\circ}$  /54 mm; refractive index (26 $^{\circ}$ ) 1.4675; IR (neat) 1660, 1600, 1330, 1270, 1220, 1160, 1095, 1038, 995, 945, 885, 812, 714  $cm^{-1}$ ; NMR  $^{19}F$  108.8 (2F), 109.2 (2F), 109.9 (2F), 114.8 (2F) and 128.8 p.p.m. (4F) ; UV  $\lambda_{max}$ . (95% EtOH) 270  $\mu m$  ( $\epsilon$  3,300), 235  $\mu m$  ( $\epsilon$  4,200) and 215  $\mu m$  ( $\epsilon$  6,500); mass spectrum  $M^+$  (510) (2 Cl) and fragment ions 491 ( $M^+-F$ ), 475 ( $M^+-Cl$ ), 460 ( $M^+-CF_2$ ), 441 ( $M^+-CF_3$ ), 383 ( $M^+-I$ ), 364 ( $M^+-FI$ ) and 348 ( $M^+-ICl$ ). Calcd for  $C_{10}F_{12}ICl$ : Cl, 6.86. Found: Cl, 6.38.

Reaction of IIIb with Potassium Iodide (100 $^{\circ}$ )

In a manner similar to that described above, 8.36g (0.02 mol) of IIIb 6.7g (0.04 mol) of KI in 35 ml of DMF was heated to 100 $^{\circ}$  for 24 h then cooled and poured into water. Ether extracts of the aqueous mixture gave after concentration a semi-solid. The liquid portion was unreacted IVb and the solid after recrystallization from *n*-hexane gave 8.4g (70%) of 2,2'-di-

iodododecafluoro-(bi-1-cyclopenten-1-yl) nc (Vb): m. p.  $52^{\circ}$ ; IR (KBr) 1640, 1570, 1320, 1265, 1240, 1205, 1155, 1085, 1020, 987, and  $805\text{ cm}^{-1}$ ; NMR  $^{19}\text{F}$  108.6 (8F) and 128.7 p.p.m. (4F); UV  $\lambda_{\text{max}}$ . (95% EtOH)  $270\ \mu\text{m}$  ( $\epsilon$  5,000)  $255\ \mu\text{m}$  ( $\epsilon$  5,800),  $243\ \mu\text{m}$  ( $\epsilon$  6,700) and  $225\ \mu\text{m}$  ( $\epsilon$  7,000); mass spectrum  $\text{M}^+$  602 and fragment ions 583 ( $\text{M}^+-\text{F}$ ), 475 ( $\text{M}^+-\text{I}$ ), 456 ( $\text{M}^+-\text{FI}$ ), 425 ( $\text{M}^+-\text{CF}_2\text{I}$ ), 406 ( $\text{M}^+-\text{CF}_3\text{I}$ ), 387 ( $\text{M}^+-\text{CF}_4\text{I}$ ) and 348 ( $\text{M}^+-2\text{I}$ ).

#### Reaction of IIIc with Butyllithium/Iodine

A solution of n-butyllithium in hexane (5.0 ml, 0.011 mol) was added from a syringe to a stirred mixture of 4.14g (0.0080 mol) of IIIc and 200 ml of dry ether cooled to  $-75^{\circ}$  and protected by a nitrogen atmosphere. After addition was complete, the reaction mixture was stirred for an additional 30 min. at  $-75^{\circ}$  then 2.20g (0.0086 mol) of iodine was added and the mixture allowed to slowly warm to room temperature. The reaction mixture was poured into water and a dark organic layer separated. The organic layer was washed with sodium bisulfite solution, dried over  $\text{MgSO}_4$  and concentrated under vacuum. VPC analysis of the residue indicated that it contained approximately 48% unreacted IIIc, 50% of the desired product and 2% of a higher boiling product.

Fractional distillation of the crude mixture gave 1-chloro-2'-iodohexadecafluoro-(bi-1-cyclohexen-1-yl) nc (IVc): b.p.  $103-105^{\circ}/26\text{mm}$ ; IR (neat) 1650, 1620, 1340, 1270, 1240, 1180, 1040, 1020, 980, 932, 867 and  $780\text{ cm}^{-1}$ ; NMR  $^{19}\text{F}$  103-143 p.p.m. complex absorption; UV  $\lambda_{\text{max}}$ . (95% EtOH) 208 ( $\epsilon$  3,700) and  $275\ \mu\text{m}$  ( $\epsilon$  1,700); mass spectrum ( $\text{M}^+$ ) 610 (1 Cl) and fragment ions 591 ( $\text{M}^+-\text{F}$ ), 575 ( $\text{M}^+-\text{Cl}$ ), 483 ( $\text{M}^+-\text{I}$ ) and 383 ( $\text{M}^+-\text{C}_2\text{F}_4\text{I}$ ). Calcd for  $\text{C}_{12}\text{F}_{16}\text{ICl}$ : Cl, 5.73. Found: Cl, 6.08.

#### Reaction of IVb with copper powder

Into a small sublimation apparatus was placed 10g of copper powder and 2.55g (5.0 mmol) of the liquid IVb containing a trace of DMF. The lower portion of the apparatus was heated by an oil bath to  $140-145^{\circ}$  for 5 h. A crystalline solid was collected from the cold finger and recrystallized from n-hexane yielding 1.8g (94%) of tetracosafuoro-2,2''-dichloro-1,1':2',1'',1'''-quatercyclo-1-pentenyl nc (VIb): m.p.  $89^{\circ}$ , IR(Nujol) 1630, 1370, 1330, 1280, 1160, 1110, 990 and  $885\text{ cm}^{-1}$ ; NMR  $^{19}\text{F}$  111.1 (4F), 113.0 (4F),

113.6 (4F), 118.0 (4F), 131.5 (4F) and 134.4 p.p.m. (4F); mass spectrum  $M^+$  766 (2 Cl) and fragment ions 747 ( $M^+-F$ ), 731 ( $M^+-Cl$ ), 716 ( $M^+-CF_2$ ), 697 ( $M^+-CF_3$ ), 681 ( $M^+-CF_2Cl$ ), 647 ( $M^+-C_2F_5$ ) and 631 ( $M^+-C_2F_4Cl$ ).

#### Reaction of Vb with copper powder

In a manner similar to that described above, a small sublimation apparatus was charged with 10g of copper powder, 2.0g (3.0 mmol) of Vb and 2 ml of DMF then heated to 140° for 24 h. A crude white crystalline product was collected from the cold finger and recrystallized from *n*-hexane yielding 1.0g (91%) of perfluoro tetracyclopentenocyclooctatetraene VIIb: m.p. 81.5°; IR (Nujol) 1660, 1380, 1340, 1280, 1180, 1085 and 1020  $cm^{-1}$ ; mass spectrum 696 ( $M^+$ ) with fragment ions 677 ( $M^+-F$ ), 646 ( $M^+-CF_2$ ), 627 ( $M^+-CF_3$ ), 608 ( $M^+-CF_4$ ) and 596 ( $M^+-C_2F_4$ ) (lit., [5] m.p. 81-82.5; IR (KBr) 1618, 1337, 1273, 1230, 1212, 1087 and 1020  $cm^{-1}$ ).

#### ACKNOWLEDGMENTS

We wish to thank the Robert A. Welch Foundation (Grant AF-585) and the AFOSR Chemical Division for their financial support of this work. We also want to thank Dr. S. W. Oh for assistance and helpful discussions in this research.

#### REFERENCES

- 1 W. R. Cullen, A. R. Davis, F. W. B. Einstein, J. D. Hazlett, A. W. Wu and Can J. Chem 1976, 54 (18) 2871
- 2 R. L. Soulen, B. T. Nakata and J. D. Park, J. Fluorine Chem., 1 (1971/72) 235
- 3 G. Camaggi, S. F. Campbell, R. D. H. Perry, R. Stephens and J. C. Tatlow, Tetrahedron, 22 (1966) 1755.
- 4 J. D. Park, S. K. Choi and G. G. Pearson, Abstracts of the 158th National Meeting of the American Chem. Soc., N. Y. Sept. 1969, FLU0 006.
- 5 R. L. Soulen, S. K. Choi and J. D. Park, J. Fluorine Chem., 3 (1973/74) 141.
- 6 G. Camaggi, J. Chem. Soc. (C), (1971) 2382.