

## 1-Chloro-2-iodoperfluorocycloalkenes 와 2, 2'-Dichloroperfluorocycloalkenyls 합성의 개량

崔 三 權 · 朴 達 祚

한국과학원 화학 및 화학공학과

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## The Improved Synthesis of 1-Chloro-2-iodoperfluorocycloalkenes and 2, 2'-Dichloroperfluorocycloalkenyls

Sam Kwon Choi and Joseph D. Park

Department of Chemical Science, Korea Advanced Institute of  
Science, Seoul, Korea

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**요 약.** 1-Chloro-2-iodoperfluorocycloalkenes 를 종전에는 DMF 용매속에서 KI 를 사용하여 Halogen 교환반응에 의하여 합성하였으나 alkyllithium 으로 금속교환반응을 통하여 iodination 함으로써 반응시간이 단축되던지 특히 1,2-dichloroperfluorocyclohexene 의 경우에는 더 높은 수득물의 1-chloro-2-iodoperfluorocyclohexene 을 얻을 수 있었다. 그리고 1,2-dihaloperfluorocycloalkenes 의 coupling 반응도 fluorocycloolefins 과 등분을 DMF 와 혼합하여 slurry 를 만들어 이것을 sublimator 속에서 감압하에 반응시키므로써 반응시간과 온도를 낮출 수 있었으며 생성물의 수득률도 많이 증가시킬 수 있었다. 대표적인 예로서 1-chloro-2-iodotetrafluorocyclobutene 의 coupling 반응에 있어서는 종전에 비해서 더 높은 수득물의 coupling product 를 얻을 수 있었다. 한편 coupling 반응이 가능한 기구를 검토하고 그 생성물의 물리적 성질을 측정하여 확인하였다.

**ABSTRACT.** The preparation of 1-Chloro-2-iodoperfluorocycloalkenes was achieved with a short reaction time and a high yield when the starting compound was iodinated via the metalation process using an alkyllithium reagent. Especially, the high yield of 1-chloro-2-iodo-perfluorocyclohexene was obtained when 1,2-dichloroperfluorocyclohexene was iodinated via the same reaction conditions. The coupling reaction of 1,2-dihaloperfluorocycloalkenes was also achieved with a lower reaction temperature and a shorter reaction time when the equal slurry mixture of fluorocycloolefines and DMF was reacted at a high pressure in a sublimator. The yield of the coupling product was greatly improved by this process. For a typical example, the coupling reaction of the 1-chloro-2-iodotetrafluorocyclobutene was proceeded with a higher yield of the product than that of the reported reaction, when the present method was adopted. A plausible reaction mechanism of the present coupling reaction was proposed and the physical characteristics of the coupling product were confirmed.

### INTRODUCTION

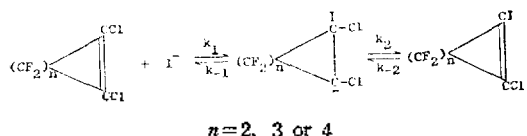
Although the preparation of 1-chloro-2-iodo

perfluorocycloalkenes has been repeatedly investigated by Moore<sup>1</sup>, McMurtry<sup>2</sup>, Nakata and Soulen<sup>3</sup>. Versions at high temperatures and along



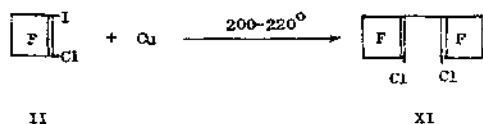
abilities" of the respective halogens from the postulated carbanion intermediate.

Nakata<sup>9</sup> discovered the halogen-metal interchange reaction of 1,2-dihalopolyfluorocycloalkenes and demonstrated the synthetic utility of these polyfluorolithio derivatives in the preparation of various 1-chloro-2-iodoperfluorocycloalkenes (Table 1).



The much improved yields of these mono-iodide substituted perfluorocycloalkenes provide alternative method to the reaction of 1,2-dichloroperfluorocycloalkenes with KI in DMF.

Choi<sup>6</sup> of this laboratory showed that an Ullman type reaction of 1-chloro-2-iodotetrafluorocyclobutene (II) with copper powder at 200~220° gave 2,2'-dichlorooctafluoro-(bi-1-cyclobuten-1-yl) (XI) in 70 % yield.



The coupling of 1,2-diiodotetrafluorocyclobutene (III) under similar conditions yielded no 2,2'-diiodooctafluoro-(bi-1-cyclobuten-1-yl) (XII) but rather, a cyclic trimer perfluorobenzo-(1,2,3,4,5,6)-tricyclobutene (XIII) was found.

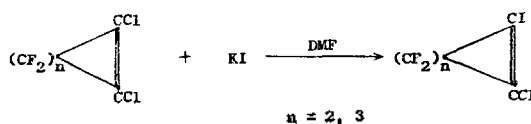
## RESULTS AND DISCUSSION

When 1-chloro-2-iodides and 1,2-diiodides of perfluorocyclobutene and perfluorocyclopentene

Table 1. Halogen-metal interchange with BuLi.

Product	$n$	% Yield
II	2	67
V	3	58
X	4	76

were prepared in DMF under conditions employed by Nakata and Soulen, a study was made to determine the temperature at which the initiation of the reaction took place. For 1,2-dichlorotetrafluorocyclobutene (I), the reaction started at about 55°, whereas the temperature for the reaction of 1,2-dichlorohexafluorocyclopentene (IV) with KI occurred at around 90°. Consequently, iodide exchange reactions of (I) and (IV) in DMF were attempted at temperatures corresponding to their initial reaction temperatures, with a one to two molar ratio of (I) or (VI) to KI. In addition to the starting material and some decomposed products, the 1-chloro-2-iodides of perfluorocyclobutene (II) and perfluorocyclopentene (V) were isolated in a considerably higher yield than before (Table 2).



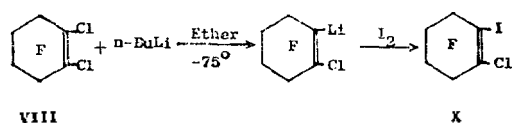
From these experimental data, it is apparent that temperature plays a rather important role in determining the distribution of the products, and if the reaction is truly an equilibrium process, the presence of a large excess of iodide ion would force the reaction to give disubstituted products.

Attempts were made to determine if 1,2-dichlorooctafluorocyclohexene (VIII) would react with potassium iodide in DMF at the temperature employed for the 1,2-dichlorides of perfluorocyclobutene (I) and perfluorocyclopentene (IV), but all efforts were fruitless

Table 2. Reaction of 1,2-dichloroperfluorocycloalkenes with KI in DMF.

Product	$n$	Temp. °C	Reaction time	% Yield
II	2	55~66	19 hrs	78
V	3	90~125	21 hrs	85

since only the starting materials were recovered. Consequently, Nakata's method<sup>9</sup> of using lithio derivatives of 1,2-dichlorooctafluorocyclohexene (VIII) was employed to synthesize the needed 1-chloro-2-iodooctafluorocyclohexene (X). The yield of monoiodide was over 80 %, however, no 1,2-diiodooctafluorocyclohexene was isolated, even with an excess of *n*-butyl-lithium and iodine.



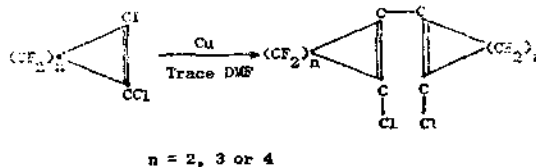
After several attempts, it appeared that the most convenient route to obtain a large amount of the dimers from 1-chloro-2-iodoperfluorocycloalkenes was by heating a mixture of fluoroolefin with copper powder in 1 to 4 ratio by weight and in the presence of 0.8 drops DMF per gram of olefin. Rapid stirring was required to prevent settling of the copper powder and better dispersion of copper throughout the medium. After the reaction mixtures thickened, they were cooled before final steps were taken to remove the products from the copper powder. It was important that care be taken to avoid overheating the reaction mixtures. When overheating happened, large amounts of decomposed products were detected.

The isolation of the pure dimeric products from the reaction mixtures required various techniques depending upon the starting olefin. The coupled product (XI) from 1-chloro-2-iodotetrafluorocyclobutene (II) was separated from the reaction mixture by replacing the reflux condenser with the appropriate sublimation apparatus, and the product sublimed under slight vacuum to yield 80 % of pure (XI).

Since 2,2'-dichlorododecafluoro-(bi-1-cyclopenten-1-yl) (XXI) is a high boiling liquid, its isolation was accomplished by extraction of the

reaction mixture with ether. The ether solution was then washed with water to remove DMF, dried over  $MgSO_4$  followed by distillation. The yield of product isolated was always above 80 %, however, some 2*H*, 2'*H*-dodecafluoro-(bi-1-cyclopenten-1-yl) (XX) was also isolated as a minor product. The unusual propensity for the five-membered ring to abstract a proton during the coupling reaction has been noted by Camaggi<sup>5</sup>.

Recovery of pure 2,2'-dichlorohexadecafluoro-(bi-1-cyclohexen-1-yl) (XXII) was accomplished by extracting the reaction mixture with *n*-hexane and removing the solvent under reduced pressure. The crude product thus isolated was easily purified by recrystallization from hexane with little contamination from other impurities.

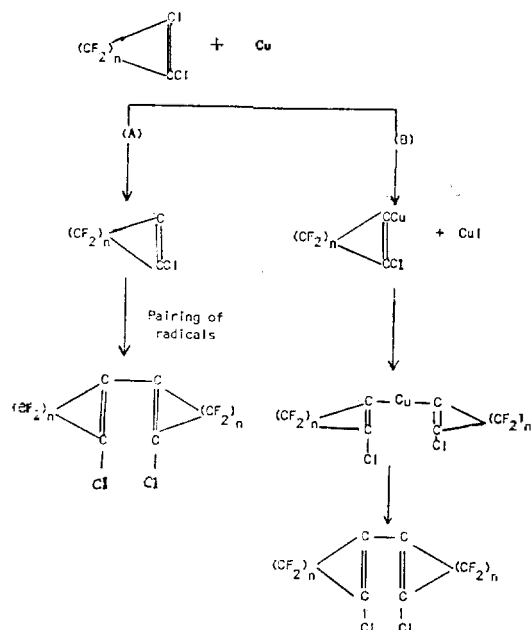


There is no conclusive evidence for the mechanism of these types of coupling reactions, but by analogy to the Ullman reactions, they may be said to undergo through an intermediate state either as (1) free radicals, (2) organometallic compounds of moderate stability, or (3) metallic complexes of transitory existence<sup>17,18</sup>. The proposed mechanism are depicted in *Scheme 2*.

The bond-breaking process occurring in chemisorption might involve successive accession of

Table 3. Copper coupling reaction of 1-chloro-2-iodoperfluorocycloalkenes.

<i>n</i>	Temp. °C	Time	% Yield
2	130~135	4.5 hrs	80
3	130~135	5.5 hrs	81
4	140~145	2 hrs	90



single electrons as in path A giving an intermediate radical; the pairing of radicals might then give the bicyclic products. Path B involves the formation of a transient organocopper intermediate. Self-coupling of such intermediate, path C, might lead to the bicyclic products. Path D involves reaction of the organocopper intermediate with alicyclic halide through a four center transition state

## EXPERIMENTAL

**Preparation of 1-Chloro-2-iodotetrafluorocyclobutene (II).** In a 2 l three-necked round-bottom flask, fitted with condenser, magnetic stir bar, thermometer and a pressure equalizing addition funnel, was placed 332 g (2.0 mol) of finely ground potassium iodide and 1 l of DMF. After all the KI was completely dissolved, a solution of 194 g (1.0 mol) of 1,2-dichlorotetrafluorocyclobutene (I) was added dropwise, accompanied by gradual raising of the temperature. The reaction mixture was stirred and

maintained at 55~60° for 19 hours. At the end of this time, the reaction mixture was cooled to room temperature and 300 ml. of H<sub>2</sub>O was added. The volatile organic compounds were then steam distilled, washed with water, and dried over anhydrous MgSO<sub>4</sub>. Fractional distillation at reduced pressure gave 215 g (75 %) of 1-chloro-2-iodotetrafluorocyclobutene (II), b. p 56°/97 mm; ir 1,580 cm<sup>-1</sup> (C=C) (lit.<sup>3</sup> b. p 54°/100 mm; ir 1,580 cm<sup>-1</sup>), and 38 g (10 %) of 1,2-diiidotetrafluorocyclobutene (III): b. p 93°/97 mm; ir 1,550 cm<sup>-1</sup> (C=C) (lit.<sup>3</sup> b. p 95°/100 mm; ir 1,550 cm<sup>-1</sup>).

**Preparation of 1-Chloro-2-iodohexafluorocyclopentene (V).** In a 2 l three-necked round bottom flask, fitted with condenser, magnetic stir bar, thermometer and pressure equalizing addition funnel, was placed 332 g (2.0 mol) of finely ground KI and 1 l. of DME. After all of the KI was completely dissolved, a solution of 244g (1.0 mol) of 1,2-dichlorohexafluorocyclopentene (IV) was added dropwise, accompanied by a gradual raise of temperature. With stirring, the reaction mixture was maintained at 90° for 19 hours and then at 125° for 2 hours. At the end of this time, the reaction mixture was cooled to room temperature and 300 ml of water was added. The products were then steam distilled, washed with water, and dried over anhydrous MgSO<sub>4</sub>. Fractional distillation at reduced pressure yielded 286 g (85 %) of 1-chloro-2-iodohexafluorocyclopentene (V): b. p 60°/97 mm; ir 1,595 cm<sup>-1</sup> (C=C) (lit.<sup>3</sup> b. p 62°/100 mm; ir 1,600 cm<sup>-1</sup>), and 25 g (10 %) of unreacted 1,2-dichlorohexafluorocyclopentene (IV).

**Preparation of 1-Chloro-2-iodooctafluorocyclohexene (X).** A solution of 20 g (0.068 mol) of 1,2-dichlorooctafluorocyclohexene (VIII) in 100 ml anhydrous diethyl ether in a 250 ml reaction vessel equipped with two reflux condensers (the first topped with a nitrogen gas inlet tube,

the other with a drying tube filled with indicating Drierite), a magnetic stirring assembly, and a serum cap was cooled to  $-75^{\circ}$  (Dry Ice-Acetone bath). *n*-Butyllithium (32 ml of 2.2 M in hexane) was added to the stirred solution in a dropwise manner by means of a syringe. After the addition was completed, the reaction mixture was stirred for an additional 30 minutes, and 3.3 g (0.034 mol) biodine was added, then slowly allowed to reach room temperature. The mixture was poured into water and washed with sodium bisulfite solution. The organic layer was separated, dried over anhydrous  $MgSO_4$  and the solvent removed in a rotatory evaporator. Distillation at reduced pressure yielded 21.0 g (80 %) of 1-chloro-2-iodooctafluorohexene (X): b. p  $79\sim 80^{\circ}/69$  mm; ir  $1,610\text{ cm}^{-1}$  (C=C) (lit.<sup>8</sup> b. p  $142^{\circ}/630$  mm; ir  $1,605\text{ cm}^{-1}$ ).

**Preparation of 2,2'-Dichlorooctafluoro-(bi-1-cyclobuten-1-yl) (XX).** In a 50 ml round-bottom flask, fitted with condenser and magnetic stir bar, was placed 80.0 g of copper powder and 20.0 g (0.07 mol) of 1-chloro-2-iodotetrafluorocyclobutene (II) containing 18 drops of DMF. The reaction vessel was heated in an oil bath to  $130\sim 135^{\circ}$  for 4.5 hours, during this time the reaction mixture turned to a slurry. This was then sublimed under reduced pressure to give 9 g (80 %) of 2,2'-dichlorooctafluoro-(bi-1-cyclobuten-1-yl) (XI): m. p  $69^{\circ}$ ; ir  $1,555\text{ cm}^{-1}$  (C=C) (lit.<sup>8</sup> m. p  $69.5\sim 70.5$ ; ir  $1,555\text{ cm}^{-1}$ ); uv max (95 % EtOH)  $298\text{ nm}$  ( $\epsilon$  2,500),  $268$  ( $\epsilon$  7,500),  $260$  ( $\epsilon$  10,200).

**Preparation of 2,2'-Dichlorododecafluoro-(bi-1-cyclopenten-1-yl) (XXI).** In a 50 ml round-bottom flask fitted with condenser and magnetic stir bar was placed 80.0 g of copper powder and 20.0 g (0.048 mol) of 1-chloro-2-iodohexafluorocyclopentene (V) containing 18 drops of DMF. With stirring, the reaction vessel was heated in an oil bath to  $130\sim 135^{\circ}$

for 5.5 hours, at which time the reaction mixture turned to a white slurry. After cooling, the reaction mixture was extracted with diethyl ether, and the ether extracts washed with water, dried over anhydrous  $MgSO_4$ , and distilled under reduced pressure to give 8.1 g (81 %) of 2,2'-dichlorododecafluoro-(bi-1-cyclopenten-1-yl) (XXI): b. p  $84\sim 86^{\circ}/59$  mm; ir  $1,650\text{ cm}^{-1}$  (C=C) and  $1,605\text{ cm}^{-1}$  (C=C) (lit.<sup>8</sup> b. p  $148.5\sim 149.0^{\circ}/618$  mm; ir  $1,650$  and  $1,600\text{ cm}^{-1}$ ); UV max (95 % EtOH)  $222\text{ nm}$  ( $\epsilon$  6,300),  $240$  ( $\epsilon$  4,000); and 1.0 g (12 %) of 2*H*,2'*H*-dodecafluoro-(bi-1-cyclopenten-1-yl) (XX): m. p  $83^{\circ}$ ; ir  $1,600\text{ cm}^{-1}$  (C=C) lit.<sup>8</sup> m. p  $84\sim 85^{\circ}$ ; ir  $1,600\text{ cm}^{-1}$ .

**Preparation of 2,2'-Dichlorohexadecafluoro-(bi-1-cyclohexen-1-yl) (XXII).** In a 50 ml round-bottom flask, fitted with condenser and magnetic stir bar, was placed 20.0 g of copper powder and 5.0 g (0.013 mol) of 1-chloro-2-iodooctafluorocyclohexene (X) containing 4 drops of DMF. With stirring, the reaction vessel was heated in an oil bath to  $140\sim 145^{\circ}$  for 2 hours, at which time the reaction mixture turned to a white slurry. After cooling, the reaction mixture was extracted with diethyl ether and the ether extracts then washed with water, dried over anhydrous  $MgSO_4$ , and the solvent removed in a rotatory evaporator until a crystalline residue obtained. Upon recrystallization from *n*-hexane, 3.0 g (60 %) of 2,2'-dichlorohexadecafluoro-(bi-1-cyclohexen-1-yl) (XXII): m. p  $51^{\circ}$ ; ir  $1,640\text{ cm}^{-1}$  (C=C) and  $1,610\text{ cm}^{-1}$  (C=C) (lit.<sup>8</sup> m. p  $51.5\sim 52.0$ ; ir  $1,650$  and  $1,610\text{ cm}^{-1}$ ); UV max  $282\text{ nm}$  ( $\epsilon$  1,630),  $205$  ( $\epsilon$  11,900).

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